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GEOCHEMISTRY OF LATERITES, STABILITY OF Al–GOETHITE, Al–HEMATITE, AND Fe³⁺–KAOLINITE IN BAUXITES AND FERRICRETES: AN APPROACH TO THE MECHANISM OF CONCRETION FORMATION

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ABSTRACT. In most lateritic weathering profiles, crystallized iron-rich oxihydroxides are found to be solid solutions of goethite–diaspore or hematite–corundum. Moreover, kaolin minerals are generally found to contain small quantities of structural iron and can also be considered as solid solutions of Fe^{3+} and Al^{3+}–kaolinite endmembers. In bauxites, ferricretes, and in the top of lateritic profiles, important nodule formation takes place. The nodule formation taking place within a kaolinite soil-matrix is always made up of Al–hematite which replaces the clay through an epigenetic relation. From nodules to pisolites, the centripetal evolution results in the formation of Al–goethite at the expense of earlier formed hematite.

The distribution of Fe^{3+}–kaolinite, Al–goethite, and Al–hematite as well as the iron and aluminum contents is controlled by silica activity, pore size distribution, and the activity of water. A model calculation, based on solid solution equilibria and minimization of the Gibbs free energy in the system Fe_2O_3–Al_2O_3–SiO_2–H_2O, is proposed. The model calculates the amounts of coexisting phases and the distribution of Al and Fe in goethite, hematite, and kaolinite. It is shown that when kaolinite controls the system, the amounts of aluminum in goethite and hematite increase when the activity of silica decreases. Also, when the water activity diminishes, the Al-content in goethite increases. For low water activities, hematite replaces goethite, while boehmite replaces gibbsite. Equilibrium conditions and element distributions are also shown to be dependent on the amounts of available water in the system so that results of calculations are compatible with natural observations.

INTRODUCTION

Under warm, humid, or semi-humid conditions such as those prevailing under tropical or mediterranean climates, red and yellow are the dominant kaolinitic soil colors. In contrast, soils of temperate regions are dominantly yellowish colored. The high chroma-colors of the lateritic soils are determined by the amounts of ferrihydrite, hematite, and goethite. Goethite is by far the most widespread form of pedogenic iron oxide and

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may originate and persist in widely diverse environments (Schwertmann, Fischer, and Taylor, 1974; Schwertmann and Taylor, 1977). The zonal and intrazonal occurrence of goethite and hematite has been documented in many places (Taylor and Graley, 1967; Schwertmann, 1969; Fölster, Noshrefi, and Ojenuga, 1971; Lamouroux, 1972; Davey, Russel, and Wilson, 1975; Nahon, 1976; Kämpf and Schwertmann, 1983).

Since Correns and Von Engelhardt (1941), Norrish and Taylor (1961), and Bardossy (1968), substitutions of Al for Fe in the structure of goethite and hematite have been found in bauxites, ferricretes, laterites, and in most of the natural profiles in which these minerals form. Correlatively, since Boesman and Schoemacker (1961) many natural kaolinites have been determined as Fe^{3+}-substituted. Amounts of iron in kaolinites are generally very small but highly dependent on the physicochemical properties of these clay minerals (Yvon and others, 1981; Cases and others, 1981).

This paper is an attempt to review the distribution, range of composition, and conditions of formation of Al–goethites, Al–hematites, and Fe^{3+}–kaolinites in natural tropical weathering profiles, including bauxites and ferricretes.

SUBSTITUTION RANGES AND METHOD OF DETERMINATION

A. Determination of the substitution of Al^{3+} for Fe^{3+} in geothites and hematites.—Measurements of the degree of substitution of Al^{3+} for Fe^{3+} in goethite and hematite have been performed by Mössbauer spectrometry since Janot and Gibert, 1970. Another method is based on the relation between shifts of X-ray diffraction peaks and degrees of substitution according to the Vegart Law (Norrish and Taylor, 1961; Thiel, 1963). Deviations from the Vegart Law have been found by Perinet and Lafont (1972a, b) and verified by Schwertmann, Fitzpatrick, and Le Roux (1977) for hematites. Parameter a can be calculated from the X-ray diffractogram, and its deviation $\Delta a(0.001 \text{ Å})$ is a function of the mole fraction of Al_2O_3 within hematite (X percent) according to the relation:

$$\Delta a = 0.022 \text{ X}^2 + 1.82 \text{ X}$$

B. Determination of the substitution of Fe^{3+} for Al^{3+} in kaolinites.— The substitution of Fe^{3+} into kaolinite has been studied by Mössbauer spectrometry (Malden and Meads, 1967; Janot, Gibert, and Tobias, 1973). It seems also that quite precise results may be obtained by Electron Spin Resonance (ESR), elsewhere called EPR or RPE. An ESR spectra of Fe^{3+}–kaolinite shows three types of signals among which two are significantly used. A first group of resonance signals is located around g = 4.67 Gauss. This group includes two main peaks called internal (S_I) and external (S_E). The amount of Fe^{3+} substituted is proportional to the sum of the areas of these two peaks ($S_I + S_E$). The kaolinite cristallinity is inversely correlated with the area of the internal peak (S_I) and positively correlated with the area of the external peak (S_E). A second peak is located around g = 2. Its intensity ($I_G = 2$) decreases when the kaolinite cristallinity diminished. The intensity ($Ig = 2$) is also influenced by small amounts of oxihydroxides.

Iron oxides or hydroxides are often associated with Fe^{3+}–kaolinite causing an enlargement of the (Ig = 2) peak. A purifying treatment removing the free oxihydroxydes (Endredy, 1963) generally shows the disappearance of this (Ig = 2) signal. Then, the iron content of the material can be considered as structural.

C. Range of aluminum and iron respectively in goethites, hematites, and kaolinites.—In natural and synthetic goethites substitutions of Al^{3+} for Fe^{3+} range from 0 to 33 percent mole fraction of AlO(OH) (Beneslavsky, 1957; Simon, Lang, and Seidel, 1959; Thiel, 1963; Petit, Backer, and Herzog, 1964; Wefers, 1967; Janot and Gibert, 1970; Solymar, 1970; Janot and others, 1971; Bardossy, 1968, 1982).

In natural and synthetic hematites, the substitutions range between 0 and 15 percent mole fraction of Al_2O_3 (Pouillard, 1950; Caillère, Gatineau, and Hénin, 1960; Shirane, Cox, and Roby, 1962; Bardossy, 1968, 1982).

In natural kaolinite, the mole fraction of Fe^{3+}–kaolinite does not exceed 3 percent according to Janot, Gibert, and Tobias (1973), Rengasamy, Krishna-Murti, and Sarna (1975), Herbillon and others (1976), Fayolle (1979), Mendelovici, Yariv, and Villalba (1979), Didier (1983), and Cantinolle and others (1983). Furthermore, Herbillon and others (1976) and Mestdagh, Vielvoye, and Herbillon (1980) have shown that an increasing substitution of iron in kaolinite induces a diminution of cristallinity and an augmentation of disordering.

In conclusion, goethites and hematites can incorporate quite large amounts of aluminum in their structures. The mole fraction of AlO(OH) in goethites appears generally greater than the mole fraction of Al_2O_3 admitted into hematites. Furthermore, the iron content in the kaolinite structure is significant but small. The degree of substitution of Al^{3+} for Fe^{3+} in goethites or hematites as well as the degree of substitution of Fe^{3+} for Al^{3+} in kaolinites is highly variable under natural conditions. Substitutions have undoubtedly a determinant role, even if it is not yet quantitatively appreciated, on the cristallinity and solubility of these minerals. Therefore, their stability fields have to be reconsidered in terms of solid solution equilibria.

DISTRIBUTION OF Al–HEMATITE AND Al–GOETHITE IN LATERITES

An abundant literature is devoted to the distribution of hematite and goethite in soils and weathering products such as bauxites, iron ferricretes, tropical kaolinitic alterations, and, more generally, laterites.

A. Bauxites.—In aluminum rich horizons and bauxites, gibbsite is generally the dominant aluminous mineral. As the formations get older boehmite progressively replaces gibbsite, and if burial or metamorphism takes place, even corundum may appear (Goldich and Berquist, 1948; Nia, 1968; Bardossy, 1982).

In most of the bauxites, Bardossy (1982) shows that hematite and goethite are often present and also that hematite dominates when boehmite is present. Furthermore, as described by Combes (1969) the classical bauxite parageneses are the following:

1. kaolinite and goethite are often closely related;
2. when gibbsite replaces kaolinite, goethite tends to be stable;
3. when boehmite, to a lesser extent, or diaspore, to a greater extent, appears, kaolinite, gibbsite, and goethite tend to disappear. Then, hematite dominates in the iron-rich phases.

Boulangé (1983) in a recent and extensive study of bauxites in the Ivory Coast, has clearly demonstrated that:

1. hematite and boehmite dominate in nodules and interglaebular plasmas of the initial aluminous ferricretes;
2. the amount of boehmite increases from the bottom to the top of the bauxitic profiles and becomes dominant in the pisolitic facies;
3. in the concretionary facies, boehmite tends to be more concentrated in the core of pisolites than in the surrounding plasma.

Cantinolle and others (1983) have analyzed the mineral assemblage of the Canonnettes bauxites (southeast of France) and have found that in the mottled kaolinitic bauxite, the cristallinity of kaolinite decreases, while iron content in kaolinite and aluminum content in the coexisting goethites increases together from the bottom to the top of the profiles.

In bauxitic formations, Norrish and Taylor (1961), Janot and Gibert (1970), Solymar (1970), Janot and others (1971), Mendelovici, Yariv, and Villalba (1979), and Bardossy (1982) have found substitutions of Al_2O_3 in hematite ranging from 4 to 14 mole percent. Furthermore, they found substitutions of $AlO(OH)$ in goethite solid solutions, ranging between 5 and 33 mole percent. The last number represents to our knowledge the highest value found in natural samples (table 1).

In bauxitic profiles, the dehydrated minerals, hematite and boehmite, tend to be associated in the core of the pisolites, whereas the hydrated minerals, goethite and gibbsite, are formed together either in the initial or in the latest stages of the development of the profiles. The Al-content of goethite or hematite increases toward the top of the weathering formations.

B. Gibbsite or kaolinite acid soils.—According to Taylor and Graley (1967) hematite dominates in the upper parts of the old profiles. Therefore, the ratio hematite/goethite increases when the temperature rises, the humidity of the climate decreases, or the aridity increases, when the soil pH increases (Kampf and Schwertmann, 1983).

Aluminum content in hematite of oxisoils analyzed by Schwertmann, Fitzpatrick, and Le Roux (1977) is reported in table 1. It is shown that the substitution is smaller in hematite than in goethite.

Fitzpatrick and Schwertmann (1982) have analyzed the aluminum content of goethites in strongly acid soils (gibbsitic soil or ferrallitic soils), moderately acid soils (kaolinitic soils or ferruginous tropical soils), and kaolinite bearing saprolites. Some geodes, mottles, or concretions were also considered. This extensive study shows clearly that the goethites of concretions, mottles, and kaolinitic, moderately acid soils are less substi-

tuted than those of kaolinitic saprolite and even less than those of strongly acid soils containing gibbsite (fig. 1).

C. *Ferricretes on lateritic profiles.*—In ferricretes, which are in a sense equivalent to bauxites, but, developed under seasonally contrasted tropical climate, hematite, goethite, kaolinite, and in many cases, quartz are often present but diversely distributed. The distribution of ferricretes as a function of time, climate, position in landscape, and nature of the parent material has been largely discussed over the past 50 yrs, among others by de Chetelat (1938), D'Hoore (1954), Maignien (1958), Millot (1964), Leprun (1971, 1972, 1979), Michel (1973) Nahon (1976), Nahon and Millot (1977), Boulet (1974), Nahon and others (1977), Didier (1983), Didier and others (1983), and Nahon (1985).

Typically, an old and well preserved lateritic weathering profile on granitic rock is represented in figure 2. Five different horizons are distinguished (Tardy, 1969; Nahon, 1976):

1. The fresh parent granitic rock.
2. The saprolite, in which, together with smectite and kaolinite, some feldspars or primary micas remain unaltered.

TABLE 1

Average aluminum content in goethite of various origins

| Formation	References	Mineral	Composition $\frac{AlO(OH)}{Al_2O_3}$ $\frac{FeO(OH)}{Fe_2O_3}$		Associated minerals
Bauxite	Norrish and Taylor (1961)	Goethite	14.5	85.5	Kaolinite, gibbsite
Bauxite	Bardossy (1968)	Goethite	17.0	83.0	Kaolinite, gibbsite, boehmite
Bauxite	Bardossy (1968)	Hematite	3.0	97.0	Kaolinite, gibbsite, boehmite
Bauxite	Janot and Gibert (1970)	Hematite	12.0	88.0	Boehmite
Bauxite	Janot and Gibert (1970)	Hematite	5.0	95.0	Kaolinite, gibbsite (or boehmite)
Bauxite	Janot and Gibert (1970)	Hematite	5.0	95.0	Kaolinite, gibbsite (or boehmite)
Bauxite	Solymar (1970)	Goethite	22.5	77.5	No records
Bauxite	Janot and others (1971)	Goethite	10.0	90.0	Kaolinite, gibbsite
Bauxite	Janot and others (1971)	Goethite	15.0	85.0	Kaolinite, gibbsite
Bauxite	Janot and others (1971)	Goethite	12.0	88.0	Kaolinite, gibbsite
Bauxite	Janot and others (1971)	Hematite	12.0	88.0	Diaspore, corindon
Bauxite	Janot and others (1971)	Goethite	25.0	75.0	Kaolinite, gibbsite, boehmite
Bauxite	Janot and others (1971)	Hematite	8.0	92.0	Kaolinite, gibbsite, boehmite
Bauxite	Fitzpatrick and Schwertmann (1982)	Goethite	24.0	76.0	Kaolinite, gibbsite
Laterite	Muller and others (1981)	Goethite	15.0	85.0	Kaolinite, gibbsite
Ferricrete	Nahon (1976)	Goethite	20.0	80.0	Kaolinite, quartz
Ferricrete	Nahon (1976)	Hematite	13.0	87.0	Kaolinite, quartz
Ferricrete	Nahon and others (1979)	Goethite	15.0	85.0	Kaolinite
Ferricrete	Nahon and others (1979)	Hematite	15.0	85.0	Kaolinite
Ferricrete	Leprun (1979)	Goethite	20.0	80.0	Kaolinite, quartz
Ferricrete	Leprun (1979)	Goethite	17.0	83.0	Kaolinite, quartz
Ferricrete	Leprun (1979)	Goethite	17.0	83.0	Kaolinite, quartz
Ferricrete	Fitzpatrick and Schwertmann (1982)	Goethite	9.0	91.0	No records
Strongly acid soils	Fitzpatrick and Schwertmann (1982)	Goethite	23.0	77.0	No records
Moderately acid soils	Fitzpatrick and Schwertmann (1982)	Goethite	7.0	91.0	No records
Saprolites	Fitzpatrick and Schwertmann (1982)	Goethite	16.0	84.0	No records
Mottles	Fitzpatrick and Schwertmann (1982)	Goethite	6.0	94.0	No records
Oxisols	Schwertmann, Fitzpatrick and Le Roux (1977)	Hematite	8.2	91.8	No records
Oxisols	Schwertmann, Fitzpatrick and Le Roux (1977)	Hematite	5.5	94.5	No records
Red soils	Torrent, Gunzman and Parra (1982)	Goethite	10.0	90.0	Kaolinite
Red soils	Torrent, Gunzman and Parra (1982)	Hematite	3.0	97.0	Kaolinite
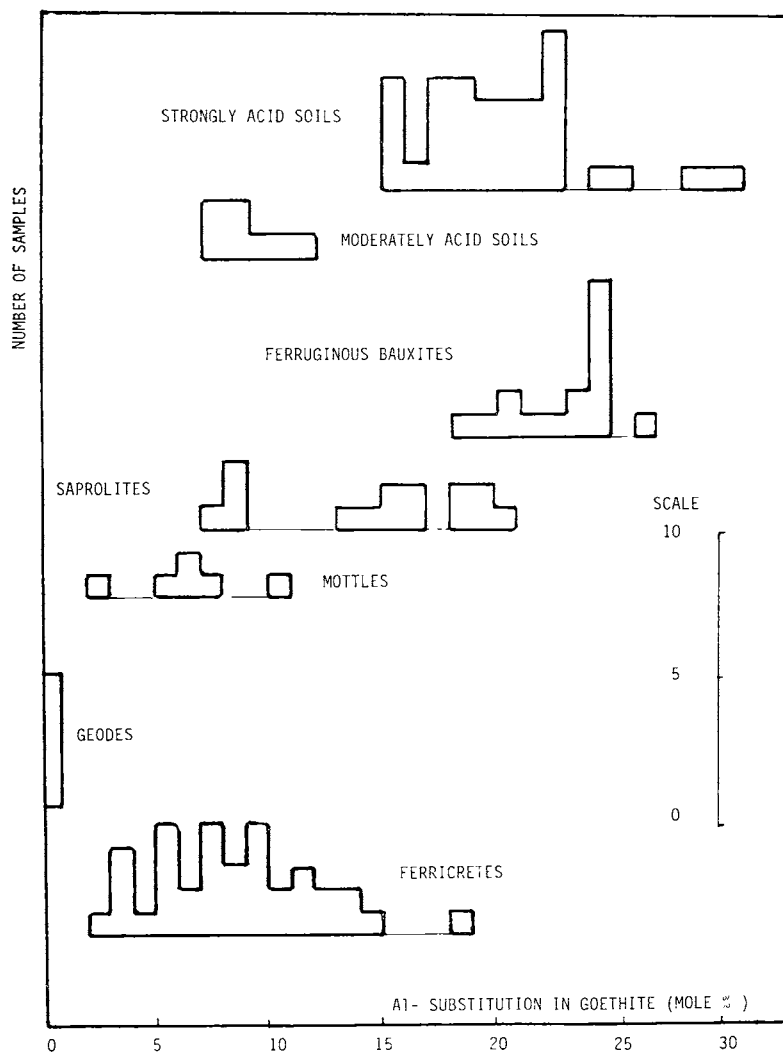
Fig. 1. Aluminum content in goethites from various origins (from Fitzpatrick and Schwertman, 1982).

3. The lithomarge, in which all primary minerals: that is plagioclases, K-spars, biotites, and amphiboles are entirely transformed into kaolinite. The initial structure of the rocks is preserved, and the isovolumetric chemical balance shows a strict conservation of aluminum and iron. Furthermore, iron is localized as goethite and located at the places previously occupied by ferro-magnesian primary minerals. Beside these pink or reddish-colored places the kaolin-transformed feldspars remain white, so that, at this level, the mobilization of iron is not yet observed. The differences

in color are determined, prior to the alteration, by the initial distribution of iron in primary minerals. The iron and color distribution are referred to as litho-relictual.

The lithomarge is then a formation in which quartz, kaolinite, and goethite coexist, all preserved along an important thickness, as long as its situation remains below the water table level.

In the saturated zone permanently located under the water table, hematite is absent, and no concretion formation is observed (Nahon, 1976; Muller and others, 1981).

4. The mottled formation overlies the lithomarge above the water table level, in the unsaturated zone. Here, progressively the initial structure of the parent rock is effaced or obliterated. Two major pedoturbations affect the mottled formation. First of all, this horizon is invaded by

GRAVELS : RESIDUAL NODULES   FERRICRETE DISMANTLING

NODULE ALTERATION

GOETHITE CORTEX AROUND

CORTIFICATION   HEMATITE NODULES

FERRICRETE

HEMATITE NODULE   FORMATION

BEGGINING OF NODULATION

MOTTLES

--ACCUMULATION OF KAOLINITE IN TUBULES
MOTTLED ZONE (KAOLINITE + GOETHITE)
IRON STARTS TO CONCENTRATE INTO
KAOLINITE-RICH SITES

ISOVOLUMETRIC LITHOMARGE
(KAOLINITE + GOETHITE)
(NO IRON MOVEMENTS OBSERVED)

SAPROLITE (SANDY)
(KAOLINITE + SMECTITE)

FRESH PARENT ROCK
(GRANITE,SANDSTONE OR BASIC ROCK)

Fig. 2. Schematic representation of a common lateritic profile and its overlying ferricrete.

a network of channels and tubular voids of large diameter (cm) in which both detrital and neoformed kaolinite can accumulate. Furthermore, iron appears now as mobilized, that is, leached from the areas located around large pores (mm) and concentrated in clay-rich areas, forming mottles, precursors of concretions. The secondary kaolinite accumulated in large tubular voids is also progressively enriched in iron so that iron concentrates in areas consisting of fine grained material characterized by a small pore size ($<<$ 0.1 mm). The original lithostructure is now progressively replaced toward the top of the profiles by a newly formed pedostructure. Here, in the mottles, goethite dominates, but hematite appears in small percentages. When mottles evolve into concretions, hematite replaces goethite.

5. The mottled formation is covered by the ferricrete sensu stricto. This horizon, generally a few meters thick, consists of an iron accumulation which can be more than 20 percent Fe_2O_3. In the middle part, cemented nodules are abundant. To the maximum in concretion formation correspond the maximum hardness and the maximum hematite development. It corresponds also to the complete replacement of the kaolinitic host by an aluminum rich hematite. Toward the top, rings of goethite appear around hematitic nodules as a secondary degradation process taking place at the edges of the large pores. The secondary goethites are formed by rehydration of Al–hematites. They are highly aluminous and become poorer and poorer in aluminum as long as the degradation process takes place. The end product is a pure goethite. Close to the top, the cohesion diminishes, and nodules have a tendency to separate from each other so that iron ferricretes are very often covered by gravels made of individual and deconsolidated nodules. Thus, the superficial gritty horizon is a result of ferricrete dismantling (Nahon, 1976). This is schematized in figure 2.

Dissolved iron moves downward from the top and accumulates in the bottom part of the crust. This movement provides iron for the concretion and nodule formation. Progressively aluminum and silicon are removed from the ferricrete; kaolinite dissolves, quartz grains are highly corroded, whereas hematite and goethite are retained and become the dominant minerals.

In conclusion, when, at the bottom of the ferricretes, goethites and hematite form together, goethite is generally of a low Al-content. This is interpreted as evidence that goethite precipitates in the large pores at the contact of the quartz grains, for instance, and that hematite forms in the smallest pores of kaolinite material which is progressively replaced and which yields the amounts of aluminum required for the Al–hematite formation.

Therefore, the highest aluminum contents in hematites are found together with the maximum development of the nodules and the maximum dissolution of kaolinite. Furthermore, the highest aluminum contents in goethites are found accompanying the first stages of rehydration of Al–hematites together with the dismantling of the nodular horizon.

D. Conclusion: field observations and distribution of Al-goethite and Al-hematite.—As seen above, hematite and goethite are often associated in tropical red soils: laterites, ferricretes, and bauxites. Hematite tends to form on the top of the profiles and in the small size pores of the unsaturated zone. Goethite tends to form at the bottom of the profiles under the water table zone. It develops also in edges of the large pores and channels which are occasionally visited by sudden water discharges. Obviously, the hematite–goethite distribution is regulated by water activity.

In addition to these general observations, it should be remarked that goethite does not replace minerals, and especially kaolinite, with which it is associated. On the contrary, hematite, when it forms instead of goethite, replaces kaolinite which dissolves. This is, in our opinion, the reason hematite concretions and nodules can be formed when the water activity of the system diminishes (fig. 3).

From natural observations, it can also be concluded that the aluminum contents of goethite and hematite should be regarded as a function of the nature of other minerals with which they are associated.

For the 183 samples analyzed by Fitzpatrick and Schwertmann (1982) and other data presented in table 1, one may underline two major facts:

1. In goethites of red soils, the substitution rates diminish when the climate becomes less humid or more arid and percolating solutions are richer in silica (Tardy, 1971).

2. Compositions range from 2 to 20 mole percent of AlO(OH) in goethites of ferricretes and other soils in which kaolinite is present. Compositions range from 18 to 27 mole percent in goethites associated with gibbsite of bauxites.
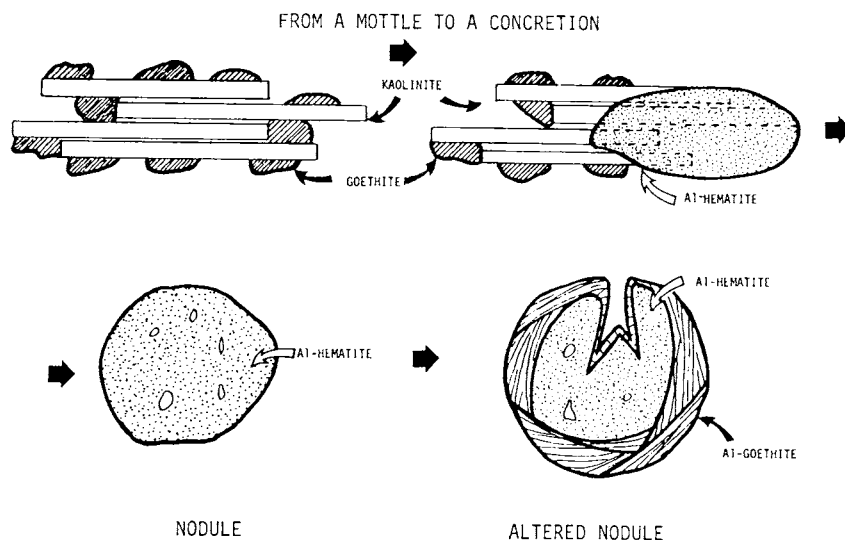
FROM A MOTTLE TO A CONCRETION

NODULE   ALTERED NODULE

Fig. 3. Formation and evolution of a mottle into a nodule and into a pseudo-pisolite (after Nahon, 1976).

Thus, the substitution rate of AlO(OH) into FeO(OH) is lower in ferricretes than in bauxites, as generally admitted by Nahon (1976), Nahon and others (1979), Leprun (1979) in laterites of Senegal and Ivory Coast. Hematite is generally substituted less than goethite, and both appear less aluminous when kaolinite and quartz are present than when gibbsite forms.

Obviously, the aluminum contents of goethites and hematites are controlled by the activity of aluminum in solution which is in turn determined by the solubility of aluminous minerals, that is, gibbsite and kaolinite.

It turns out that the relative stability fields of goethite and hematite may depend on their degree of Al-substitution which are dependent on the stability of the other aluminous minerals with which they are associated. The conditions of formation of goethite and hematite may be ultimately determined by the activity of silica in solution and by the activity of water in pores in which these minerals form.

FACTORS CONTROLLING THE FORMATION OF GOETHITE AND HEMATITE

A large number of works have been devoted, over the last 20 yrs, to the stability of iron oxides and hydroxides in the laboratory and under natural conditions (Schwertmann, 1965; Schmalz, 1959, 1968; Berner, 1969; Bischoff, 1969).

Three kinds of factors are generally considered: grain size effects, kinetics of precipitation, and equilibrium conditions involving the activity of water. Because of its importance, water activity is discussed in a separate section. In the present section only grain size effects and kinetics are treated.

A. Grain size effect.—Langmuir (1971) has treated this problem extensively and has shown that the relative stability of Al-free goethite and hematite in water is strongly dependent on the particle size of the minerals involved. Because the heats of dissolution as a function of particle size are different for goethite and hematite, the equilibrium reaction energy is also a function of the dimensions of the crystals. When crystals of hematite and goethite are of the same size, hematite appears to be more stable than goethite. This is also, of course, true when hematite crystallizes in a larger size. However, the opposite is observed when hematite forms in a smaller grain size than goethite.

In the cases of ferricretes, two situations are observed. In the first steps of the formation of mottles and concretions, hematite and goethite are both of a small size, and there is difficulty in saying which is coarser than the other. During the last steps of nodule dismantling, only, the secondary goethite appears in quite well formed crystals of about 1 μm diameter.

Because hematite and goethite in concretions and nodules never show large crystals but only very tiny particles of about 100 Å in diameter, it seems clear that conditions governing their stability must be related more to dehydration and water activity and less to particle size effects.

B. The kinetic interpretation.—The hematite and goethite formation mechanism in soils has been discussed by Schwertmann and Taylor (1977). Kampf and Schwertmann (1983) have written that "Iron from silicates and other primary sources released into solution may lead to a direct crystallization of goethite if the solubility product of goethite, but not the much higher one of ferrihydrite, is exceeded. If the solubility product of ferrihydrite is exceeded however, ferrihydrite will be formed and may then transform either to hematite via a dehydration, or alternatively to goethite via dissolution of ferrihydrite". One may understand here that the primary factor that governs the rate of dissolution versus precipitation of iron is kinetic. Then, these authors continue their interpretation and state that factors favoring hematite over goethite formation are those that favor ferrihydrite formation such as a rapid release of Fe and a low concentration of organic compounds which complex Fe, thereby allowing a somewhat higher concentration of inorganic Fe^{3+} ions. Conversely organic compounds favor goethite formation, because the Fe-complex formation prevents the attainment of ferrihydrite saturation.

In addition, once ferrihydrite is formed, hematite is favored over goethite with increasing temperature because dehydration is involved in the ferrihydrite → hematite transformation.

This interpretation is based fundamentally on laboratory experiments and statistical correlations between mineralogical data and a set of environmental factors. Kämpf and Schwertmann (1983) themselves have recognized: "the hematite–goethite relationship cannot be elucidated from our study, however, because of the strong intercorrelation among factors considered such as temperature, excess of moisture and even soil organic matter and pH".

Berner (1969), reviewing the stability conditions of hematite in water, has pointed out that, although hematite is more stable than goethite, kinetic phenomena may be the reason for the non-spontaneous formation of hematite in water. Slow transformation of original metastable goethite should take place during diagenesis, and this is the probable reason why goethite is absent in buried sediments ranging from Tertiary to Paleozoic in age (Fischer, 1963). Langmuir (1969) is in agreement with Berner's (1969) view that fine-grained goethite has no thermodynamic stability relative to well crystallized hematite. Then, for kinetic reasons, goethite is more common than hematite, and also for kinetic reasons, once hematite has appeared, it does not rehydrate to form coarse goethite.

However, natural observations made on ferricrete suggest that besides the kinetic interpretation, the distribution of goethite and hematite can also be understood in terms of thermodynamic equilibria in which the chemical potential of water is involved.

ACTIVITY OF WATER, PORE SIZE EFFECT, AND CONCRETION FORMATION

A. Activity of water (a_w).—By definition, the activity a_i of any substance, subscribed as i (Garrels and Christ, 1965), is defined as:

$$a_i = f_i/f^\circ_i$$

in which f_i and $f°_i$ stand respectively for the fugacity of the vapor above the substance, and $f°_i$ the fugacity of the vapor when the substance is in its standard state. For water vapor in the atmosphere, at room temperature, and under normal atmospheric total pressures, fugacities can be regarded as equal to partial pressures, so that:

$$a_w = p/p_o = R.H./100$$

in which p and p_o stand respectively for the water partial pressure above the soil and the water partial pressure of the corresponding water-saturated air. R.H. (percent) is then the relative humidity of the air measured at a given temperature and pressure.

In porous media and in the unsaturated zone of soils, the activity of capillary water, retained behind the concave meniscii, is equal, if equilibrium is reached, to the relative humidity of the air imposed by climatic conditions (see Hillel, 1971; or Sposito, 1981).

When rainfall ceases, the water percolation stops, and after drainage and evaporation, water is retained in pores of progressively smaller and smaller radii and consequently behind smaller and smaller air-water interface meniscii. As a result, water activity also diminishes progressively (see Bourrié and Pédro, 1979; Dandurand and others, 1982). The Laplace's formula allows calculation of the pressure difference between the two sides of the air-water interface as a function of σ, the interfacial tension (72.7 dyn/cm at 25°C for pure water) and r the radius of the circular section of the pore:

$$\Delta P = -2 \sigma/r$$

The change in the chemical potential of the water is a function of its molar volume ($\bar{V}$) and the pressure difference (ΔP) between each side of the meniscus:

$$(\mu - \mu_o) = RT \ Ln \ a_w = \bar{V}.\Delta P = -\bar{V}.2 \ \sigma/r$$

In all cases of capillary waters, these terms are all negative because ΔP is negative. The scale of correspondence between the size of cylindrical shaped pores and the activity of water is given in table 2. It is interesting to remark that a relative humidity of 0.5, commonly observed during the dry season of tropical climates, corresponds to a pore diameter of about 30 Å which is precisely the diameter of pores provided by the edges of kaolinite grains.

B. Hydration-dehydration isotherms and the pore diagram of kaolinite.—Petrographic observations have shown that hematite concretions form preferentially in sites previously enriched in kaolinite and not in sites previously leached and made of quartz skeleton only.

The question that emerges concerns the pore size distribution offered by kaolinite aggregates compared to that shown by quartz grain assemblages. The pore size distribution can be calculated from adsorption or desorption isotherms, assuming that the pore shape is known. In the literature, most of the BET surface areas and pore size distributions are

TABLE 2

Correspondence between the diameter of the meniscus (or capillary)
and the equilibrium water activity

	Pore diameter	Activity of water
d =	30 μm (3 × 10^{-5}m)	a_w = 0.99993
d =	3 μm (3 × 10^{-6}m)	a_w = 0.9993
d =	0.03 μm (3 × 10^{-8}m)	a_w = 0.9312
d =	0.003 μm (3 × 10^{-9}m)	a_w = 0.4903
d =	0.0003 μm (3 × 10^{-10}m)	a_w = 0.0009
d(m) =	− 0.0921 10^{-8}/log a_w	

based on nitrogen adsorption, and only a few are derived from water
adsorption or desorption. Depending on the type of molecule used (N_2 or
H_2O) the results may be different particularly concerning pores of very
small size (several Å). Because natural processes occur in water media, we
have performed and selected a series of measurements and calculations
devoted to water adsorption or desorption on kaolinite.

Kaolinite isotherms have been presented by Keenan, Mooney, and
Wood (1951), Torrence-Martin (1958), and Kehres (1983). An example
taken from Kehres (1983) is shown in figure 4. It concerns a Georgia
kaolinite. A dehydration isotherm is a curve obtained by plotting θ, the
water content (grams of H_2O per gram of dry clay) as a function of water
activity (a_w). The activity of water is defined as the ratio $a_w = p/p_o$; p is
the equilibrium partial pressure of vapor at a given stage of hydration,
and p_o is the equilibrium partial pressure at saturation (pure liquid water
in standard state).

From the data of the dehydration isotherm (right side of fig. 4), two
kinds of results are derived. The first concerns the BET surface area, and
the second the pore size distribution. The BET surface area (Brunauer
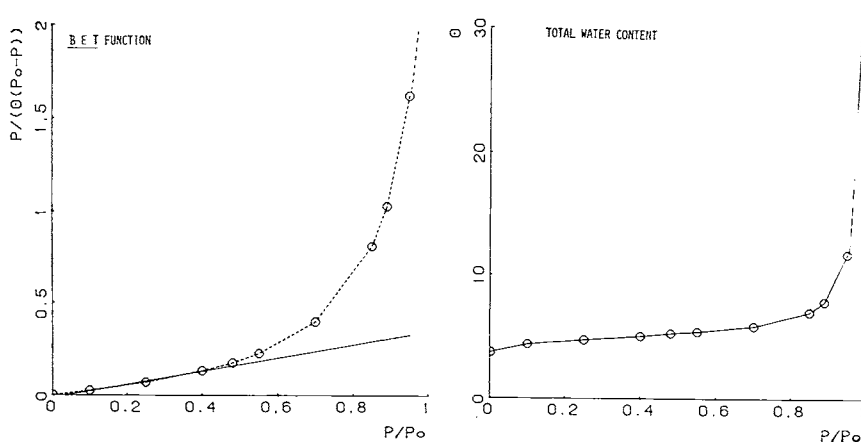
Fig. 4. Dehydration isotherm and BET surface area of kaolinite (after Kehres, 1983).

and Emett, 1935, 1937; Brunauer, Emett, and Teller, 1938) is obtained by plotting $p/(\theta(p_o-p))$ as function of $a_w = p/p_o$ (left side of fig. 4). Between $p/p_o = 0.1$ and 0.4 the function is linear, so that:

$$p/(\theta(p_o-p)) = \alpha\,(p/p_o) + \beta$$

and the BET theory says that:

$$\alpha = \frac{C-1}{V_m C} \text{ and } \beta = \frac{1}{V_m C}$$

By knowing α and β, it is possible to calculate C, a function of the energy of adsorption, and V_m, the volume of a monolayer adsorbed. The surface area A is easily calculated from the monolayer volume V_m. The Georgia kaolinite studied presents a BET surface area of about 35 m²/g. Clay minerals such as disordered kaolinites may present a quite large surface area mostly due to defects of layer stacking. Then, an important part of the surface area is created along the edges, in pores of small size.

The pore size distribution can be calculated by following two methods. The first is based on the application of Kelvin's formula for cylindrical pores (Pierce, 1953). Another method is used here in order to take into account that clay minerals are planar layers and that pores should have planar walls instead of cylindrical ones (Delon and Dellyes, 1967).

Pierce's method for pores of cylindrical shape is based on the following approach. For a given p/p_o, θ is the volume of water per gram of dry clay trapped in pores of a diameter smaller than d.

To an increment $\Delta(p/p_o)$ corresponds a volume change $\Delta\theta$ and an internal area, change ΔA. The average pore diameter $\bar{d}$ concerned is included between d and d $+$ Δd, and one defines a distribution function $S(\bar{d})$:

$S(\bar{d}) = \Delta A/\bar{d}$, for internal $\Delta(p/p_o)$;

$S(\bar{d})$ is in fact constant up to a given length l and in the case of a cylinder;

$S(\bar{d}) = \pi\bar{d}l/d = \pi l$.

The Delon-Dellyes's (1967) method considers pores of parallel planar faces. The Kelvin's relationship has a different formulation, but the pore distribution function, $S(\bar{d})$ is calculated similarly:

$$S(\bar{d}) = \Delta A/\bar{d}$$

$\bar{d}$ is the average distance between the planar face concerned by the corresponding surface area ΔA. The numbers given in ordinate axes in figure 5 correspond in fact to additions of pore length 10^{20} Å per gram of clay calculated per intervals of radius or diameter (Δd), derived from intervals of water activity $\Delta(p/p_o)$.

The distribution function $S(\bar{d})$ calculated from Pierce's method corresponds to a summation of real pore length, because these pores are considered as cylindrical. The distribution function $S(\bar{d})$ calculated from

Delon-Dellyes's method is derived from the same equation and also has the dimension of a length [L]. However, it does not correspond to a real summation of pore length, because the pores are supposed, in this case, to be of a planar shape.

The two diagrams of figure 5, characterizing a Georgia kaolinite studied by Kehres (1983), present almost the same distribution function. The maximum of the length distribution is obtained for a pore radius of about 20 Å (let us say 21 Å) or a pore diameter of about 40 Å (let us say 42 Å) which corresponds to an average of six 7 Å–kaolinite layers.

By comparison between kaolinite aggregates and quartz powder of about the same grain size (2-4 μm) the surface area of a disordered kaolinite is, in general, much greater (35 m²/g instead of 5 m²/g), and the pores of small size ($<$ 50 Å in diam) are much more numerous in kaolinite than in quartz.

C. Porosity differences between kaolinite cutans and quartz sands.— In tropical soils, there are domains enriched in kaolinite coexisting with zones in which quartz sand dominates. The former correspond to areas of parent material initially enriched in biotite and amphibole or to cutans made by illuviation and accumulation of fine grained material. The latter correspond to areas of parent material initially rich in quartz or to eluviated zones from which kaolinite has been leached.

At low water activities, kaolinitic cutans may retain much more water than quartz sand, simply because the proportion of small pores is quite high at the edges of kaolinite crystals and extremely low at the contact between quartz grains. At high water activities, the contrary is observed,
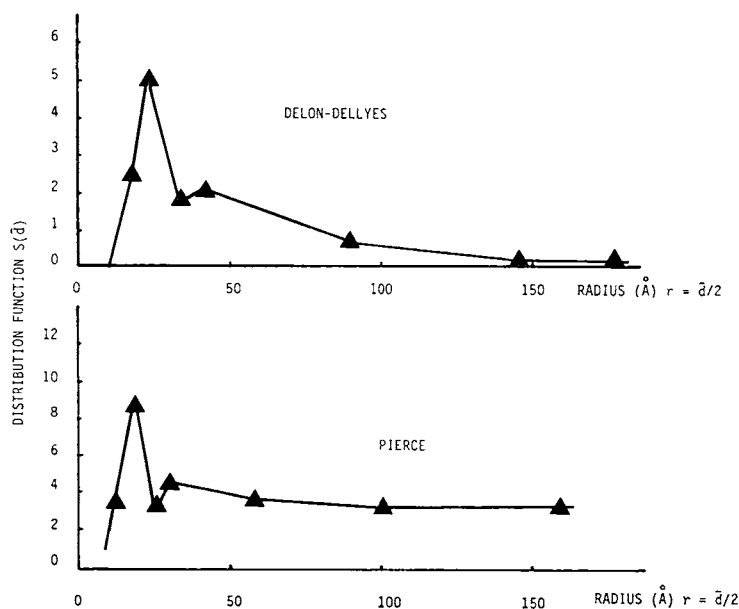
Fig. 5. Pore diagram of kaolinite (after Kehres, 1983).

and the porosity of quartz sand filled by water could be very large. It seems not unreasonable to expect that solutions that become saturated with respect to iron minerals should precipitate goethite in water of high activity at the contact with large sized pores and hematite in water of low activity in very small sized pores. Therefore, another mechanism should take place and explain formation of goethitic mottles and the development of the hematitic nodules and concretions.

D. Mottles, concretions, and nodule formation.—One of the most remarkable facts in the process of a ferricrete formation is that iron is leached from large sized pores and accumulates in small sized pores, that is, moves from sand to clay.

This process starts to take place above the water level and develops farther toward the soil surface. Under the water table, in the permanently wet horizons, no migrations are observed.

Above the water table level, mottles begin to form, and the first mineral that concentrates is goethite. Farther upward, hematite follows goethite, and nodules develop from mottles. In both cases, iron moves from the outer part to the inner part of the concretion. The driving force of this migration and accumulation seems to be the initial difference in the size of the pores which tends to be accentuated as the concretion develops. The interpretation of this phenomenon was proposed by Tardy and Monnin (1983) who have calculated the mineral solubility differences as functions of the size of the pores in which they precipitate. Briefly, these authors have proposed that an aqueous solution at saturation with respect to a given mineral in a pore of a large size can be oversaturated with respect to the same mineral in a pore of small size. In other words, water circulating in large channels dissolves minerals, becomes saturated with respect to them, and fills the pores of small size. After drainage, the small sized pores remain filled by water retained behind concave miniscii of small radii. In these conditions, the solutions become oversaturated with respect to the corresponding minerals which precipitate and tend to fill the porosity which again decreases in size; thus, the initial process is perpetuated.

Two reasons may be responsible for these changes in the saturation state of solutions. The first corresponds to the changes in the activity of solids as a function of the shape of their surface. An activity of unity characterizes pure phases presenting infinite and flat surfaces. An activity greater than unity characterizes generally pure phases presenting convex interfaces behind which the pressure is locally greater than in the external domain. In such cases, solids are more soluble than they are in their standard state. An activity smaller than unity characterizes generally pure phases presenting concave interfaces behind which the pressure is locally smaller than in the external domain. Solids are, then, less soluble in such cases than they are in their standard state (Wollast, 1971). This is the reason a solid surface presenting needles and cracks evolves naturally and becomes flat: needles dissolve, and cracks are filled. Iler (1979) has shown that such a mechanism is responsible for the evolution of silica-gels, where-

as Tardy and Monnin (1983) and Dandurand and others (1982) have proposed that it is responsible for the formation of silica concretions and for silcrete formation.

The second phenomenon acting in the same way takes place when, after drainage, water remains, behind concave meniscii, in pores of small size. Here, in water, the pressure is smaller than in the atmosphere, and the activity of water is smaller than unity. Tardy and Monnin (1983) have proposed that minerals that are more soluble when pressure increases would be less soluble when pressure decreases, that is, behind concave meniscii. In fact, Dandurand and others (1982) have verified that aqueous silica concentration at equilibrium with respect to amorphous silica diminishes when the pores concerned become smaller and smaller.

Iron minerals, such as goethite and hematite, also follow these rules and are both more soluble when particle size decreases and when pressure increases.

These different mechanisms all act in favor of a concentration of goethite and hematite in pores of small size and in favor of the mottle formation concretioning and nodulation. When the size of pores in which the precipitation reaction takes place, that is, when the activity of water is small enough, goethite no longer forms, and hematite becomes the dominant mineral. A decrease of the activity of water is not only responsible for concretion formation but also for the nature of the mineral formed.

EQUILIBRIUM REACTIONS AS FUNCTIONS OF WATER AND SILICA ACTIVITIES

Because goethite and hematite are respectively hydrated and dehydrated minerals, their equilibrium boundary is first of all dependent on the activity of water. Also, because Al–goethite is a solid solution of diaspore and goethite and Al–hematite a solid solution of corundum and hematite, the chemical compositions of the coexisting solid solutions are controlled by water activity in the system Al_2O_3–Fe_2O_3–SiO_2–H_2O. Furthermore, because kaolinite interferes in the control of Al ions in solution, the chemical compositions of goethite and hematite are also dependent on the activity of dissolved silica.

A. Solubility products of minerals.—In the following sections we have used conventional aqueous species for writing equilibrium equations and calculating solubility products of the following minerals:
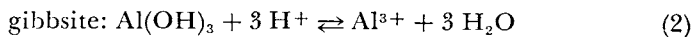
$$\text{diaspore or boehmite: } AlO(OH) + 3\ H^+ \rightleftarrows Al^{3+} + 2\ H_2O$$

and

$$\log [Al^{3+}]/[H^{3+}] + 2 \log [H_2O] = \log K_{sp} \text{ diaspore}$$

$$\tfrac{1}{2} \text{ corundum: } \tfrac{1}{2}\ Al_2O_3 + 3H^+ \rightleftarrows Al^{3+} + 1.5\ H_2O \tag{1}$$
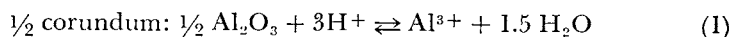
and

$$\log [Al^{3+}]/[H^+]^3 + 1.5 \log [H_2O] = \log K_{sp} \tfrac{1}{2} \text{ corundum}$$

$$\text{gibbsite: } Al(OH)_3 + 3\ H^+ \rightleftarrows Al^{3+} + 3\ H_2O \tag{2}$$

and

$$\log K_{sp} \text{ gibbsite} = \log [Al^{3+}]/[H^+]^2 + 3 \log [H_2O]$$
$$\tfrac{1}{2} \text{ kaolinite: } \tfrac{1}{2}\ Al_2Si_2O_5(OH)_4 + 3\ H^+ \rightleftarrows Al^{3+} + SiO_2 + 2.5\ H_2O$$

$$\text{(3)}$$

and
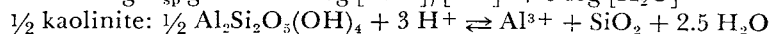
$$\log K_{sp} \text{ ½ kaolinite} = \log [Al^{3+}]/[H^+]^3 + \log [SiO_2] + 2.5 \log [H_2O]$$

$$\text{goethite: } FeO(OH) + 3H^+ \rightleftarrows Fe^{3+} + 2 H_2O \tag{4}$$

and

$$\log [Fe^{3+}]/[H^+]^3 + 2 \log [H_2O] = \log K_{sp} \text{ goethite}$$

$$\text{½ hematite: } \text{½ } Fe_2O_3 + 3H^+ \rightleftarrows Fe^{3+} + 1.5 H_2O \tag{5}$$

and

$$\log [Fe^{3+}]/[H^+]^3 + 1.5 \log [H_2O] = \log K_{sp} \text{ ½ hematite}$$

$$\text{quartz: } SiO_2 \rightleftarrows SiO_{2(aq)} \tag{6}$$

and

$$\log [SiO_2] = \log K_{sp} \text{ quartz} \tag{7}$$

B. A thermodynamic and solubility product data set.—The Gibbs free energies of formation and the solubility products of minerals used are reported in tables 3 and 4. They include data presented by Robie and Waldbaum (1968), Langmuir (1969), Naumov, Ryzhenko, and Khodakovsky (1971), Berner (1971), Hem (1970), Hem and Roberson (1967), Hem and Lind (1974), Hem and others (1973), Parks (1972), Ulbrich and Merino (1974), Helgeson and others (1978), Hemingway, Robie, and Kittrick (1978), Robie, Hemingway, and Fischer (1978), Khodakovsky (1983, personal commun.).

The solubility product values of minerals and of the endmembers involved in the solid solutions were discussed by Fritz and Tardy (1974), Fritz (1981), Tardy and Fritz (1981), Tardy (1982), and Didier (1983). In fact, when looking at the stability field of minerals in nature, it appears that the solubility product values listed in table 4 are not all internally consistent and are not capable of illustrating correctly the observed mineral associations and the Al/Fe ratios in goethite and hematite natural solid solutions.

We started from the solubility products of gibbsite (8.205) and kaolinite (7.41) chosen by Fritz and Tardy (1974). These values are compatible with the fact that quartz and kaolinite coexist and have been chosen over the years as the "best values" for kaolinite and gibbsite formed in laterites.

The solubility product of boehmite is derived from the data of Robie, Hemingway, and Fischer (1978), by subtracting from our gibbsite K_{sp} value the same difference as found in column 8 of table 4:

$$\log K_{sp} \text{ boehmite} = \log K_{sp} \text{ gibbsite} + 0.14 = 8.205 + 0.14 = 8.345 \tag{8}$$

Other values were adapted in order to be compatible with natural observations and the ideal solid solution model. These numbers are reported in the last columns of tables 3 and 4. It seems clear that goethite, hematite, and diaspore solubility products are higher than those currently

quoted in the literature. This is supported by the fact that the solid solutions found in nature are crystallizing in a very small size and should be more soluble than the corresponding well crystallized minerals.
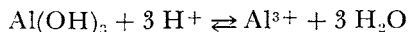
C. Gibbsite-kaolinite equilibrium.—The solubility products of kaolinite and gibbsite are written as follows:

$$\tfrac{1}{2}\,Al_2Si_2O_5(AH)_4 + 3\,H^+ \rightleftarrows Al^{3+} + SiO_{2(aq)} + 2.5\,H_2O$$
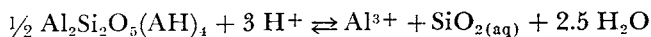
with

$$\log\,[Al^{3+}]/[H^+]^3 = +3.705 - \log\,[SiO_{2(aq)}] - 2.5\,\log\,[H_2O] \qquad (9)$$

and

$$Al(OH)_3 + 3\,H^+ \rightleftarrows Al^{3+} + 3\,H_2O$$

with

$$\log\,[Al^{3+}]/[H^+]^3 = 8.205 - 3\,\log\,[H_2O] \qquad (10)$$

in which the terms between brackets designate activities of substances. At equilibrium between the two minerals, one has:

$$\log\,[SiO_{2(aq)}] = -4.5 + \tfrac{1}{2}\,\log\,[H_2O] \qquad (11)$$

When water activity is equal to one, it becomes:

$$\log\,[SiO_{2(aq)}] = -4.5 \qquad (12)$$

If the water activity diminishes, the activity of silica defined at equilibrium also diminishes and kaolinite becomes more stable. This has been already pointed out by Sposito (1981), Pédro and Delmas (1980), and Tardy (1982) and explains why at the same level of a profile kaolinite remains stable in the finely porous materials while gibbsite is stabilized at the edges of channels and large cavities.

D. Al–goethite–kaolinite and Al–hematite–kaolinite equilibria.— When kaolinite coexists with Al–goethite or Al–hematite, the equilibrium reactions should involve diaspore and corundum components. An Al–goethite $(Al_x\,Fe_{1-x})O(OH)$ is in fact a solid solution of x $AlO(OH)$ and $(1-x)FeO(OH)$, corresponding to x diaspore and $(1-x)$ goethite mole fractions.

An Al–hematite $(\tfrac{1}{2}\,(Al_y\,Fe_{1-y})_2O_3$ is in fact a solid solution of $y(0.5\,Al_2O_3)$ and $(1-y)(0.5\,Fe_2O_2)$, corresponding to y 0.5 corundum and $(1-y)$ 0.5 hematite. Equilibria among solid solutions can be written by using partial equilibrium conditions (Fritz, 1981).

The solubility product of diaspore is written as follows:

$$AlO(OH) + 3\,H^{3+} \rightleftarrows Al^{3+} + 2\,H_2O$$
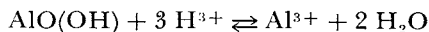
$$\log\,[Al^{3+}]/[H^+]^3 = 8.949 - 2\,\log\,[H_2O] \qquad (13)$$

When $AlO(OH)$ is involved in Al–goethite solid solution $((Al_x\,Fe_{1-x})O(OH))$, x, being the diaspore mole fraction and λ_x the corresponding activity coefficient, one has:

$$\log\,[Al^{3+}]/[H^+]^3 = 8.949 + \log x + \log \lambda_x - 2\,\log\,[H_2O] \qquad (14)$$

If the solid solution is ideal, $\lambda_x = 1$.

TABLE 3

Gibbs free energies of formation of minerals and aqueous species used. Selected data in this work are listed in column (11)

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
Fe^{3+}	−10.54	−17.87	−10.54	---	---	---	−4.60	−4.60	−4.60	----	−4.60
Fe_2O_3	−743.62	−742.41	−740.98	---	---	---	−745.40	−742.68	−728.07	----	−711.113
$FeO(OH)$	---	−490.36	−488.27	---	---	---	---	−488.55	−483.471	----	−474.305
Al^{3+}	−485.34	−492.00	−481.16	−481.16	−485.34	−485.34	−489.36	−489.40	−489.90	−489.40	−489.400
Al_2O_3	−1581.89	−1557.28	−1581.97	---	−1582.39	---	−1568.25	−1582.23	−1597.37	−1581.08	−1580.406
$AlO(OH)$ (d)	---	−921.32	−914.62	---	−918.39	−916.50	−913.78	−922.00	−921.30	−920.80	−912.702
$AlO(OH)$ (b)	---	---	---	---	−915.04	−907.30	---	−918.40	---	−915.30	−916.149
$Al(OH)_3$	−1144.28	−1156.89	−1144.32	−1139.30	−1151.85	−1147.08	−1155.48	−1154.89	−1153.98	−1154.50	−1154.138
$Al_2Si_2O_5(OH)_4$	−3777.61	−3778.15	−3776.90	−3753.05	---	−3779.95	−3789.08	−3799.36	−3789.64	---	−3789.374
SiO_2 (q)	−856.25	−856.51	−856.05	−856.88	---	−856.21	−856.25	−856.29	−856.29	---	−856.29
SiO_2 (aq)	−842.24	−833.70	−834.37	−833.95	---	−833.37	−833.41	−833.72	−833.72	---	−833.459
H_2O	−237.19	−237.19	−237.19	−237.19	−237.19	−237.19	−237.19	−237.14	−237.19	---	−237.190

(1) Robie, and Waldbaum (1968)
(2) Naumov, Ryzhenko, and Khodakovsky (1971)
(3) Berner (1971)
(4) Hem (1970); Hem, and Lind (1974); Hem, and Roberson (1973); Hem, and others (1973)
(5) Parks (1972)
(6) Ulbrich and Merino (1974)

(7) Helgeson (1978)
(8) Hemingway, Robie, and Kittrick (1978); Robie, Hemingway, and Fischer (1978); Hemingway, and Robie (1977a,b)
(9) Tardy (1982)
(10) Khodakovsky (1983)
(11) Proposed in this study

TABLE 4

Solubility products log (K_{sp}) derived from the Gibbs free energies of table 3. The values proposed in this study are given in column (11). See legend to table 3 for references corresponding to each column

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
Goethite FeO(OH)	---	- 1.331	- 0.586	---	---	---	- 4.323	- 1.696	- 0.806	---	+ 0.819
Hematite $\frac{1}{2}$ (Fe$_2$O$_3$)	- 0.962	- 0.425	- 0.729	---	---	---	- 2.161	- 1.943	- 0.663	---	+ 0.846
Diaspore AlO(OH)	---	+ 7.890	+ 7.169	---	+ 7.239	+ 7.570	+ 8.922	+ 7.318	+ 7.324	+ 7.528	+ 8.949
Boehmite AlO(OH)	---	---	---	---	+ 7.826	+ 9.180	---	+ 7.931	---	+ 8.474	+ 8.345
Gibbsite Al(OH)$_3$	+ 9.218	+ 8.177	+ 8.480	+ 9.359	+ 7.892	+ 8.728	+ 7.961	+ 8.071	+ 8.230	+ 8.140	+ 8.205
Corundum $\frac{1}{2}$ (Al$_2$O$_3$)	+11.721	+11.721	+ 8.519	---	+ 8.746	---	+10.688	+ 9.451	+ 8.124	+ 9.552	+ 9.633
Kaolinite $\frac{1}{2}$ (Al$_2$Si$_2$O$_5$(OH)$_4$)	+ 5.561	+ 5.561	+ 3.514	+ 5.228	---	+ 3.802	+ 3.714	+ 2.853	+ 3.705	---	+ 3.705

The solubility product of corundum is written as follows:

$$\log [Al^{3+}]/[H^+]^3 = 9.633 - 1.5 \log [H_2O] \qquad (15)$$

When Al_2O_3 is involved in an Al–hematite solid solution $(0.5(Al_y Fe_{1-y})_2O_3)$ y, being the corundum mole fraction, and λ_y, the corresponding activity coefficient. One has:

$$\log [Al^{3+}]/[H^+]^3 = 9.633 + \log y + \log \lambda_y - 1.5 \log [H_2O] \qquad (16)$$

If the solid solution is ideal, $\lambda_y = 1$.

The equilibrium reaction of kaolinite with pure diaspore yields:

$$\tfrac{1}{2} Al_2Si_2O_5(OH)_4 \rightleftarrows AlO(OH) + SiO_{2\,(aq)} + \tfrac{1}{2} H_2O$$
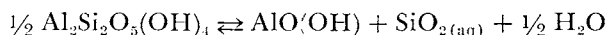
with

$$\log [SiO_2] = 3.705 - 8.949 - \tfrac{1}{2} \log [H_2O] = 5.244 - \tfrac{1}{2} \log [H_2O] \quad (17)$$

When the activity of water decreases, $\log [SiO_2]$ corresponding to the equilibrium diaspore–kaolinite increases while $\log [SiO_2]$ corresponding to the equilibrium gibbsite–kaolinite decreases. When $\log [H_2O] = - 0.744$, gibbsite and diaspore are in equilibrium, so that $\log [SiO_2] = - 4.87$ in both cases. An increase in the water activity favors gibbsite on the one hand and acts to the detriment of diaspore or boehmite on the other. The equilibrium conditions, when ideal Al–goethite $(\lambda = 1)$ and kaolinite coexist together, are those given by equalizing the expression $\log [Al^{3+}]/[H^+]^3$ in eqs (9) and (14):

$$\log [Al^{3+}]/[H^+]^3 \text{ in aqueous solution} = 3.705 - \log [SiO_2] - 2.5 \log [H_2O]$$

$$= 8.949 + \log x - 2 \log [H_2O]$$

So that:

$$\log x = - 5.244 - \log [SiO_2] - 0.5 \log [H_2O] \qquad (18)$$

When the water activity is equal to one, and at the equilibrium with kaolinite and quartz $(\log [SiO_2] = - 4)$, the AlO(OH) mole fraction is calculated as follows:

$$\log x = - 5.244 + 4 = - 1.244$$

$$x = 0.06, \text{ corresponding to } (Al_{0.06} Fe_{0.94})O(OH)$$

If we suppose that the equilibrium between Al–goethite, kaolinite, and quartz is realized in a dry environment $([H_2O] = 0.8; - 0.5 \log [H_2O] = - 0.194)$

$$\log x = - 5.244 + 4 + 0.194 = - 1.05$$

$$x = 0.08$$

It corresponds to $(Al_{0.08} Fe_{0.92})O(OH)$. As the activity of water or the activity of silica decreases, Al-content in goethite increases.

For a given water activity, x increases as the activity of silica decreases; for a given activity of silica, x increases as the water activity decreases.

The equilibrium conditions when Al–hematite and kaolinite coexist are written, according to eqs (9) and (16), as follows:

$$\log\,[Al^{3+}]/[H^+]^3 \text{ in aqueous solution} = 3.705 - \log\,[SiO_2] - 2.5\,\log\,[H_2O]$$

$$= 9.633 + \log\,y - 1.5\,\log\,[H_2O]$$

Then

$$\log\,[SiO_2] + \log\,y + \log\,[H_2O] = -\,5.928$$

For water activity equal to the unity ($\log\,[H_2O] = 0$) and if one supposes that quartz is controlling the silica activity ($\log\,[SiO_2] = -\,4$) then:

$$\log\,y = -\,1.928$$

$$y = 0.01$$

Hematite is almost pure: $(Al_{0.01}\,Fe_{0.99})_2\,O_3$.

If activities of water and silica decrease together, and if for example, $\log\,[H_2O] = -\,0.14$ (equilibrium gibbsite–boehmite) and if $\log\,[SiO_2] = -\,4.87$ (equilibrium kaolinite–gibbsite–boehmite) then, $\log\,y$ becomes:

$$\log\,y = -\,0.918 \text{ corresponding to: } (Al_{0.12}\,Fe_{0.88})_2O_3\,.$$

When the silica and water activities decrease, the amount of aluminum in hematite increases. Furthermore, when silica activity becomes too low, kaolinite is no longer stable and the amounts of aluminum in goethite and hematite are only controlled by water activity.

E. Gibbsite, boehmite, Al–goethite, and Al–hematite equilibrium conditions.—The equilibrium reactions between gibbsite, boehmite, and diaspore yield the following conditions. When boehmite forms:

$$Al(OH)_3 \rightleftarrows AlO(OH) + H_2O$$

$$\log\,[H_2O] = 8.205 - 8.345 = -\,0.14$$

$$[H_2O] = 0.72$$
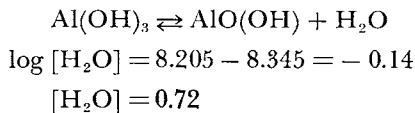
When the activity of water is sufficiently low, boehmite, instead of gibbsite, is supposed to be formed. If the water activity diminishes further, corundum forms:

$$AlO(OH) \rightleftarrows \tfrac{1}{2}\,Al_2O_3 + \tfrac{1}{2}\,H_2O$$

$$\tfrac{1}{2}\,\log\,[H_2O] = 8.205 - 9.633 = -\,1.428$$

$$[H_2O] = 0.04$$
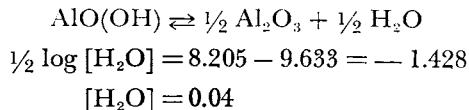
Corundum may form in very dry environments ($a_w < 0.04$). However, such a very low value is probably never reached in soils, and consequently corundum does not appear as a low temperature mineral. Furthermore, diaspore appears as less stable than boehmite. The transformation of gibbsite into diaspore involves the following conditions:

$$Al(OH)_3 \rightleftarrows AlO(OH) + H_2O$$

$$\log\,[H_2O] = 8.205 - 8.949 = -\,0.744$$

$$[H_2O] = 0.18$$
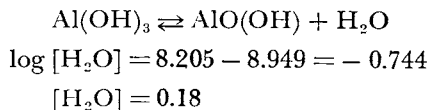
However, if diaspore appears as an endmember taking part in an Al–goethite ideal solid solution, we may have at equilibrium with gibbsite (eqs 3 and 14):

$$\log [Al^{3+}]/[H^+]^3 \text{ in aqueous solution} = 8.949 + \log x - 2 \log [H_2O]$$

$$= 8.205 - 3 \log [H_2O]$$

So that, at equilibrium:

$$\log x = -0.744 - \log [H_2O]$$

In humid conditions, water activity is equal to unity ($\log [H_2O] = 0$). The mole fraction of diaspore in Al–goethite at equilibrium with gibbsite is fixed:

$$\log x = -0.744$$

$$x = 0.18, \text{ corresponding to } (Al_{0.18} Fe_{0.82})O(OH)$$

In dryer conditions, when gibbsite transforms to boehmite, the activity of water is lower ($\log [H_2O] = -0.14$). Then, the mole fraction of diaspore in goethite is also fixed. It is, therefore, not dependent upon the water activity:

$$\log x = \log K_{sp} \text{ boehmite} - K_{sp} \text{ diaspore}$$

$$\log x = -0.604$$

$$x = 0.25, \text{ corresponding to } (Al_{0.25} Fe_{0.75})O(OH)$$

When at equilibrium with boehmite, the water activity decreases, the amounts of aluminum in goethite or hematite also increase.

Four situations are represented in the equilibrium diagrams of figure 6. When iron is not represented in the system, the three straight lines delineate a field corresponding to an undersaturated solution in which the three minerals gibbsite, kaolinite, and quartz are unstable. The positions of the equilibrium straight lines of gibbsite and kaolinite depend only on the activity of water (fig. 6A and B). When iron is present in the system, Al–goethite (fig. 6C) or Al–hematite (fig. 6D) may form. These two minerals fall in the stability field occupied by undersaturated solutions. For a given activity of water the amount of substitution of the diaspore component in Al–goethite or the corundum component in Al–hematite both diminish when $\log [Al^{3+}]/[H^+]^3$ decreases (fig. 6C and D).

F. Al–goethite and Al–hematite equilibrium conditions.—In the case of ideal solid solutions, the equilibrium conditions when Al–goethite and Al–hematite are together in equilibrium are written as follows. For $(Al_x Fe_{1-x})O(OH)$ and $Al_y Fe_{1-y})O_{0.15}$, the two partial equilibrium reactions are (eqs 1, 2, 14, and 16):

$$\log [Al^{3+}]/[H^+]^3 = \log K_{sp} \text{ diaspore} - 2 \log [H_2O] + \log x$$

$$= \tfrac{1}{2} \log K_{sp} \text{ corundum} - \tfrac{3}{2} \log [H_2O] + \log y$$
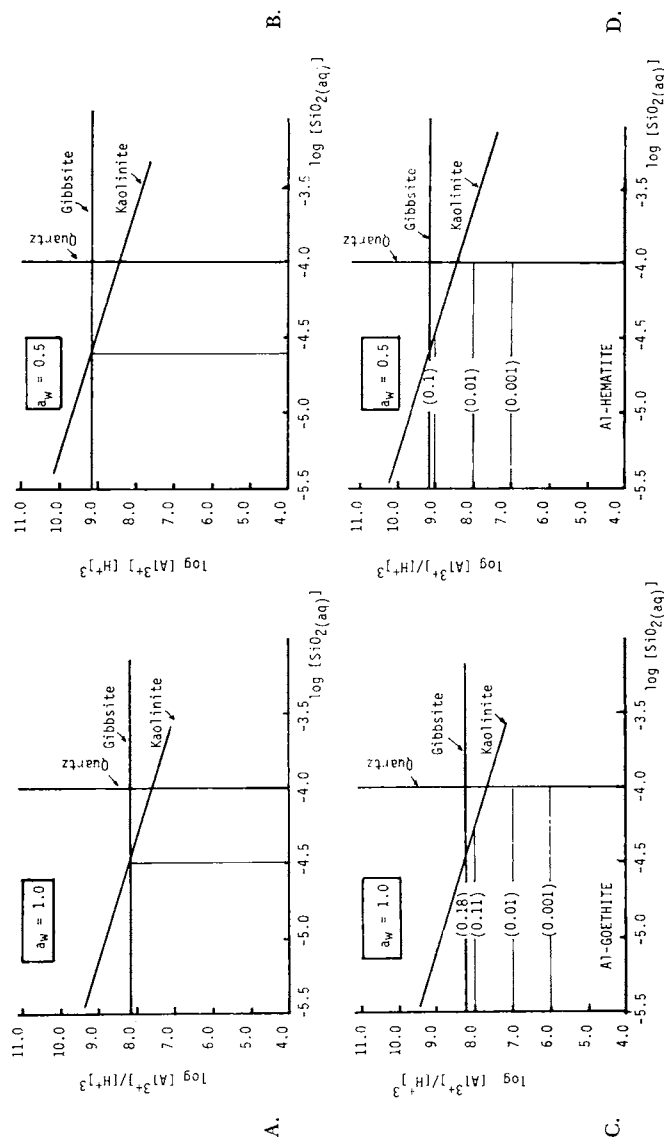
together with (eqs 5 and 6):

Fig. 6. Equilibrium diagrams of kaolinite, gibbsite, Al–goethite, and Al–hematite in four different cases: (A) $a_w = 1$ and no iron in the system; (B) $a_w = 0.5$ and no iron in the system; (C) $a_w = 1$ and Al–goethite forms; (D) $a_w = 0.5$ and Al–hematite forms. The tie-lines represent the mole fractions of the diaspore component in Al–goethite (C) or the mole fraction of the corundum component in Al–hematite (D).

$$\log [Fe^{3+}]/[H^+]^3 = \log K_{sp} \text{ goethite} - 2 \log [H_2O] + \log (1-x)$$

$$= \tfrac{1}{2} K_{sp} \text{ hematite} - \tfrac{3}{4} \log [H_2O] + \log (1-y)$$

x and y are functions of the water activity

$$\log x/y = \tfrac{1}{2} \log K_{sp} \text{ hematite} - \log K_{sp} \text{ goethite} + \tfrac{1}{2} \log [H_2O]$$

and

$$\log (1-x)/(1-y) = \log K_{sp} \text{ diaspore} - \tfrac{1}{2} \log K_{sp} \text{ corundum} + \tfrac{1}{2} \log [H_2O]$$

When the water activity diminishes, the mole fractions of goethite and diaspore diminish: x and y are determined by solving simultaneously the two equations. The amounts of Al–goethite and Al–hematite depend on the amounts of Al and Fe in the system.

For pure diaspore and corundum: x = 1 and y = 1, the equilibrium condition yields, as already shown

$$\tfrac{1}{2} \log [H_2O] = \log K_{sp} \text{ diaspore} - \tfrac{1}{2} \log K_{sp} \text{ corundum}$$

$$= 8.949 - 9.633 = - 0.684$$

$$[H_2O] = 0.21$$

For pure goethite and hematite: x = 0 and y = 0. The equilibrium condition is the following

$$\tfrac{1}{2} \log [H_2O] = \log K_{sp} \text{ goethite} - \tfrac{1}{2} \log K_{sp} \text{ hematite}$$

$$= + 0.819 - 0.846 = - 0.027$$

$$[H_2O] = 0.88$$

The dehydration of goethite into hematite appears at higher water activities than for the dehydration of diaspore into corundum. A decrease in water activity, when the two solid solutions are in equilibrium, must induce an increase of the aluminum content in Al–hematite. Furthermore, in contradiction to the model proposed by Yapp (1983), it is evident that the two solid solutions in equilibrium cannot show the same composition. The substitution rates of Fe by Al are obviously different in the two minerals and are changing as functions of the water activity and the composition of the system.

G. *Fe³+–kaolinite.*—The solubility product equations of kaolinite and Fe³+–kaolinite are written as follows

$$\tfrac{1}{2} Al_2Si_2O_5(OH)_4 + 3 H^+ \rightleftarrows Al^{3+} + SiO_{2(aq)} + \tfrac{5}{2} H_2O$$

$$\log [Al^{3+}]/[H^+]^3 + 2 \log [SiO_2] + 2.5 \log [H_2O] = 3.705$$

and

$$\tfrac{1}{2} Fe_2Si_2O_5(OH)_4 + 3H^+ \rightleftarrows Fe^{3+} + SiO_{2(aq)} + \tfrac{5}{2} H_2O$$

$$\log [Fe^{3+}]/[H^+]^3 + 2 \log [SiO_2] + 2.5 \log [H_2O] = - 3.027$$

The solubility of Fe^{3+}–kaolinite is derived from Tardy (1982). It may be calculated in order to satisfy the equilibrium between a 1 percent Fe^{3+}–kaolinite in equilibrium with a 20 percent Al–goethite. This is what is observed in lithomarges where kaolinite and goethite coexist. For a Fe^{3+}–kaolinite solid solution $((Fe_z^{3+} Al_{1-z}^{3+}) Si_2O_5(OH_4)$ one obtains:

$$\log [Fe^{3+}]/[Al^{3+}] = \tfrac{1}{2} \log K_{sp} Fe^{3+}\text{–kaolinite} - \tfrac{1}{2} \log K_{sp} \text{ kaolinite}$$
$$+ \log (z/(1-z))$$

one finds:

$$\log [Fe^{3+}]/[Al^{3+}] = -1.823 - 3.705 + \log (z/(1-z))$$
$$= -5.528 + \log (z/(1-z))$$

At the equilibrium with an Al–goethite solid solution for which x = 0.2, $(1-x) = 0.8$, one has:

$$\log [Fe^{3+}]/[Al^{3+}] = 0.819 - 8.949 + \log (x/(1-x))$$
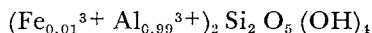$$= -8.130 + 0.602 = -7.528$$

and

$$\log (z/(1-z)) = -7.528 + 5.528 = -2$$

In that case:

$$z = 0.01$$

This corresponds to the Fe^{3+}–kaolinite formula:

$$(Fe_{0.01}^{3+} Al_{0.99}^{3+})_2 Si_2 O_5 (OH)_4$$

At equilibrium with an Al–goethite of a given composition, the amount of Fe^{3+} in kaolinite should increase when the kaolinite cristallinity diminishes, that is, when the kaolinite solubility increases.

The distribution of Al and Fe in kaolinite, goethite, and hematite has been calculated by the use of a computer program called MINEQ. This program is based on the minimization of the Gibbs free energies of the systems of a given composition and is discussed in the next section.

AN IDEAL SOLID SOLUTION MODEL DISTRIBUTION OF PHASES BY THE GIBBS FREE ENERGY MINIMIZATION

On the basis of equilibrium, the element distribution among phases and solid solutions can be calculated by using a method of minimization of Gibbs free energy. A corresponding computer program called MINEQ was designed by Perret (1983), Perret, Fritz, and Tardy (1984) and applied by Didier (1983) to the system SiO_2–Al_2O_3–Fe_2O_3–H_2O. The distribution of the elements among solid solutions is calculated on the basis of ideal mixing and as a function of element composition and water activity. All the data presented refer to 1 mole of Fe_2O_3. The amounts of Al_2O_3 and SiO_2 change from one set to another. The amount of water is limited or unlimited depending on the capability of profiles to be either closed or open for circulating water. In the first case, water activity should be lower

than unity. In the second case, it can be unity (saturated regime) but also lower than unity (unsaturated regime).

The K_{sp} and the corresponding Gibbs free energies used in the model are those of table 4, column 11, and table 3, column 11, respectively.

A. A sample calculation.—A sample calculation, in the system Fe_2O_3–Al_2O_3–H_2O is given as follows. The molal composition

$$Fe_2O_3 = 1 \qquad (Fe = 2)$$

$$Al_2O_3 = 0.1 \qquad (Al = 0.2)$$

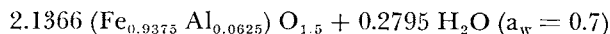$$SiO_2 = 0$$

$$H_2O = \infty$$

$$a_w = 0.7$$

can be distributed among an infinite number of mineral assemblages of various compositions, but only one assemblage and composition correspond to equilibrium. The calculated equilibrium distribution is the following:

$$0.5582 \ (Fe_{0.859} \ Al_{0.141})O(OH) + 1.5775 \ (Fe_{0.965} \ Al_{0.035})O_{1.5}$$
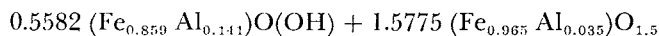
The ΔG of the system based on ideal solid solutions yields:

$$\Delta G \text{ system} = 0.5582 \ \Delta G_f{}^\circ \ Al\text{-goethite} + 1.5775 \ \tfrac{1}{2} \ Al\text{–hematite}$$

$$= -885.558 \ kJ/mole$$

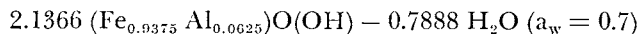Two other assemblages listed below are among many stoichiometrically equivalent. They are, for instance, either:

$$2.1366 \ (Fe_{0.9375} \ Al_{0.0625}) \ O_{1.5} + 0.2795 \ H_2O \ (a_w = 0.7)$$

for which

$$\Delta G \text{ system} = -885.500 \ kJ/mole$$

or:

$$2.1366 \ (Fe_{0.9375} \ Al_{0.0625})O(OH) - 0.7888 \ H_2O \ (a_w = 0.7)$$

for which:

$$\Delta G \text{ system} = -885.382 \ kJ/mole$$

ΔG of the system is at a minimum only for the composition corresponding to equilibrium.

Furthermore, the elemental and mineral distributions satisfy the following equilibrium relations (from eqs 5 and 6):

$$\log \ [Fe^{3+}]/[H^+]^3 \ (goethite) = \log \ [Fe^{3+}]/[H^+]^3 \ (\tfrac{1}{2} \ hematite)$$

$$= \log X + \log K_{sp} \ goethite - 2 \log \ [H_2O] = 1.113$$

$$= \log Y + \log K_{sp} \ \tfrac{1}{2} \ hematite - 1.5 \log \ [H_2O] = 1.113$$

Also, from eqs 1, 2, 13, and 15, the equilibrium conditions are satisfied:

$$\log \ [Al^{3+}]/[H^+]^3 \ (diaspore) = \log \ [Al^{3+}]/[H^+]^3 \ (\tfrac{1}{2} \ corundum)$$

$$= \log (1-X) + \log K_{sp} \text{ diaspore} - 2 \log [H_2O] = 8.407$$

$$= \log (1-Y) + \log K_{sp} \tfrac{1}{2} \text{ corundum} - 1.5 \log [H_2O] = 8.407$$

B. Data obtained in an excess of water.—In table 5, the results are shown for an excess of water so that the activity is equal to unity. For one mole of Fe_2O_3, the number of moles of Al_2O_3 changes from 0 to 1, and the number of moles of SiO_2 varies from 0 to 0.25.

All the results presented are based on 1 mole of Fe_2O_3, that is, 2 atoms of Fe. If, for example, aluminum in the systems is given as $Al_2O_3 = 0.1$, the number of atoms of $Al = 0.2$, and the mole fractions are respectively equal to:

$$Al = \frac{0.2}{0.2 + 2} = 0.0909 \text{ and } Fe = \frac{2}{0.2 + 2} = 0.9091$$

It is seen that hematite never forms in such conditions. Furthermore, quartz appears when silica content increases and when the system is poor in alumina. If the aluminum content increases over 0.10, gibbsite is formed, and consequently the amount of aluminum in goethite remains constant $(Fe_{0.82} \, Al_{0.18})O(OH)$. If silica and alumina increase together, kaolinite forms. Furthermore, if for a given amount of alumina (0.25), silica increases, the amount of kaolinite increases, the amount of goethite formed increases, but the Al substitution rate in goethite decreases.

In table 6 the reported results are obtained also for an excess of water of activity lower than unity ($a_w = 0.7$). A similar picture is reached. However for low aluminum and for high silica contents, hematite tends to form instead of goethite. Therefore, goethite or a goethite and hematite mixture inhibit gibbsite formation up to an Al_2O_3 content equal to 0.5. Here, the quantities of gibbsite formed are lower than in the previous case. Furthermore, the substitution rate of goethite by diaspore is higher in water of low activity than in water of high activity.

One can note that the differences in free energy are very low, on the order of a few hundreds of Joules. This is the reason the calculations presented in tables 5 and 6 may suffer some discrepancies. The compositions calculated are not precise, and the calculation procedure may still be improved.

Some of these results are reported on figure 7 where for one mole of Fe_2O_3, the composition and the stability fields of the hematite and goethite solid solutions are reported as functions of the water activity and aluminum content. In such conditions of excess water, hematite does not appear as associated with gibbsite or boehmite. This is observed also when the amount of water is reduced.

C. Results obtained when the amount of water is limited.—If we suppose, for example, that the porosity of the material equal to 40 percent is closed and that this porosity is initially filled by water, then the hydrated mineral formation (gibbsite, goethite) is limited, and the stability field of hematite is considerably enhanced. However, hematite and gibbsite do not coexist. If the activity of water decreases and if the water con-

TABLE 5

Composition and quantity of Al–goethite and Al–hematite associated with gibbsite, kaolinite, and quartz for various SiO_2 or Al_2O_3 content (1 mole of Fe_2O_3, $a_w = 1$ and excess of water)

Al_2O_3 / SiO_2	0.00	0.05	0.10	0.25	0.50	1.00
0	2 FeOOH	2.10 $(Fe_{0.95}Al_{0.05})$OOH	2.20 $(Fe_{0.91}Al_{0.09})$OOH	2.47 $(Fe_{0.81}Al_{0.19})$OOH 0.03 G	2.47 $(Fe_{0.81}Al_{0.18})$OOH 0.53 G	2.47 $(Fe_{0.81}Al_{0.18})$OOH
0.05	2 FeOOH 0.05 Q	2.10 $(Fe_{0.95}Al_{0.05})$OOH 0.05 Q	2.15 $(Fe_{0.93}Al_{0.07})$OOH 0.03 K	2.44 $(Fe_{0.82}Al_{0.18})$OOH 0.03 K	2.44 $(Fe_{0.82}Al_{0.18})$OOH 0.03 K 0.50 G	2.44 $(Fe_{0.82}Al_{0.18})$OOH 0.03 K 1.50 G
0.10	2 FeOOH 0.10 Q	2.10 $(Fe_{0.95}Al_{0.05})$OOH 0.10 Q	2.13 $(Fe_{0.94}Al_{0.06})$OOH 0.02 Q	2.41 $(Fe_{0.83}Al_{0.17})$OOH 0.05 K 0.04 K	2.44 $(Fe_{0.82}Al_{0.18})$OOH 0.05 K 0.46 G	2.44 $(Fe_{0.82}Al_{0.18})$OOH 0.04 K 1.46 G
0.25	2 FeOOH 0.25 Q	2.10 $(Fe_{0.95}Al_{0.05})$OOH 0.25 Q	2.13 $(Fe_{0.94}Al_{0.06})$OOH 0.17 Q 0.04 K	2.25 $(Fe_{0.89}Al_{0.11})$OOH 0.13 K	2.44 $(Fe_{0.82}Al_{0.18})$OOH 0.13 K 0.30 G	2.44 $(Fe_{0.82}Al_{0.18})$OOH 0.13 K 1.30 G

TABLE 6

Composition and quantity of Al–goethite and Al–hematite associated with gibbsite, quartz, and kaolinite for various SiO_2 or Al_2O_3 content (1 mole of Fe_2O_3, $a_w = 0.70$ and excess of water)

Al_2O_3 SiO_2	0.00	0.05	0.10	0.25	0.50	1.00
0	2 $FeO_{1.5}$	0.37 $(Fe_{0.87}Al_{0.13})OOH$ 1.73 $(Fe_{0.97}Al_{0.03})O.$	1.34 $(Fe_{0.87}Al_{0.13})OOH$ 0.86 $(Fe_{0.97}Al_{0.03})O_{1.5}$	2.50 $(Fe_{0.80}Al_{0.20})OOH$	2.70 $(Fe_{0.74}Al_{0.26})OOH$ 0.30 G	2.70 $(Fe_{0.74}Al_{0.26})OOH$ 1.30 G
0.05	2 $FeO_{1.5}$ 0.05 Q	2.04 $(Fe_{0.98}Al_{0.02})O_{1.5}$ 0.03 K	0.86 $(Fe_{0.87}Al_{0.13})OOH$ 0.64 $(Fe_{0.97}Al_{0.03})O_{1.5}$ 0.03 K	2.44 $(Fe_{0.82}Al_{0.18})OOH$ 0.03 K	2.70 $(Fe_{0.74}Al_{0.26})OOH$ 0.03 K 0.25 G	2.70 $(Fe_{0.74}Al_{0.26})OOH$ 0.03 K 1.25 G
0.10	2 $FeO_{1.5}$ 0.10 Q	2.04 $(Fe_{0.98}Al_{0.02})O_{1.5}$ 0.03 K 0.04 Q	2.15 $(Fe_{0.93}Al_{0.07})OOH$ 0.03 K 0.04 Q	2.41 $(Fe_{0.83}Al_{0.17})OOH$ 0.05 K	2.70 $(Fe_{0.74}Al_{0.26})OOH$ 0.05 K 0.20 G	2.70 $(Fe_{0.74}Al_{0.26})OOH$ 0.05 K 1.20 G
0.25	2 $FeO_{1.5}$ 0.25 Q	2.04 $(Fe_{0.98}Al_{0.02})O_{1.5}$ 0.03 K 0.19 Q	2.15 $(Fe_{0.93}Al_{0.07})OOH$ 0.03 K 0.19 Q	2.25 $(Fe_{0.89}Al_{0.11})OOH$ 0.13 K	2.70 $(Fe_{0.74}Al_{0.26})OOH$ 0.13 K 0.04 G	2.70 $(Fe_{0.74}Al_{0.26})OOH$ 0.13 K 1.04 G

MOLE FRACTION
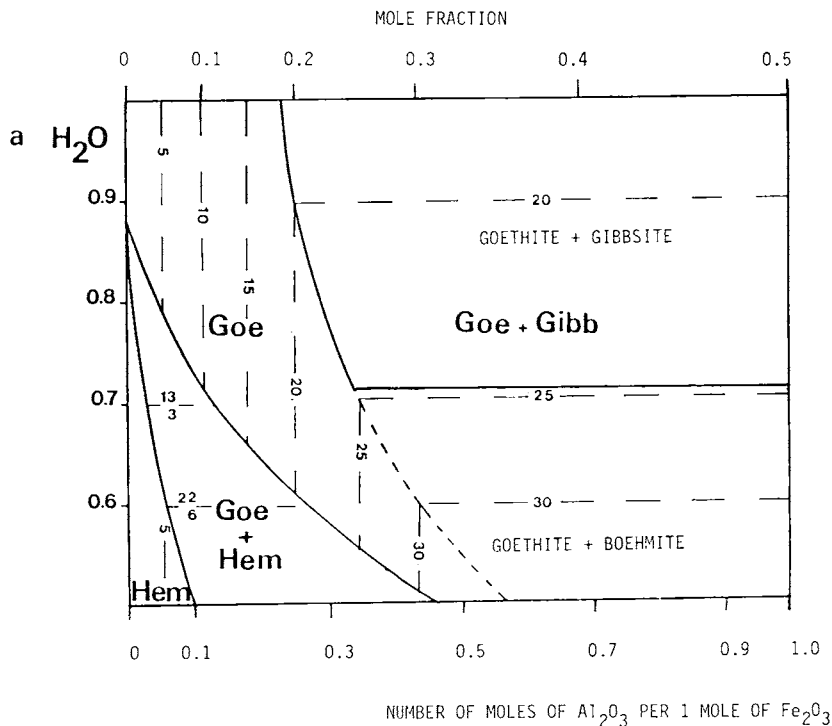

Fig. 7. Stability field of Al–goethite and Al–hematite as a function of water activity and Al_2O_3 content in the system Al_2O_3–Fe_2O_3–H_2O. Tie-lines represent the mole fraction of diaspore in goethite or corundum in hematite.

tent diminishes, gibbsite is no longer stable with respect to boehmite, and goethite no longer stable with respect to hematite. Furthermore, for relatively low Al_2O_3 contents, Al–goethite or Al–hematite can be more stable than gibbsite or boehmite, so that no aluminum phase can crystallize. The model confirms also that, when kaolinite is present together with goethite or hematite, the amount of aluminum substituted in the oxide or the oxi hydroxide decreases when the silica activity increases. The paragenesis indicates that the only free aluminum phase associated with hematite should be boehmite. When gibbsite and boehmite are excluded, goethite and hematite coexist; their aluminum content increases with the total aluminum content in the system; therefore, the substitution rate of corundum in hematite is always lower than the substitution rate of diaspore in goethite.

CONCLUDING REMARKS

The question of the equilibrium conditions in soils, as functions of water activity and the amount of available water, has been discussed by Chesworth (1972, 1975) for the system SiO_2–Al_2O_3–Fe_2O_3–H_2O with emphasis on gibbsite and boehmite stability. The gibbsite-kaolinite equilib-

rium has been analyzed by Mattigod and Kittrick (1980), Pédro and Delmas (1980), Sposito (1981), and Tardy (1982). The diminution of the water activity due to the transition from the saturated regime to the unsaturated one is clearly realized to be an important factor, which can be responsible for phase boundary displacement.

From careful petrographic observations made on the distribution of goethite and hematite in ferricretes and lateritic red soils, conclusions may be drawn.

1. Goethite commonly forms in young bauxitic profiles and is preserved in the lower parts of the old bauxitic formations. Here, goethite and gibbsite coexist in a very common lateritic paragenesis. Furthermore, when, in the old bauxites, boehmite can take the place of gibbsite, hematite forms instead of goethite.

2. Goethite is also the dominant ferric mineral in the permanently humid tropical red or yellow lateritic soils in which kaolinite dominates. Here, the typical paragenesis is quartz, kaolinite, and goethite. The iron oxihydroxide is intimately associated with kaolinite, forming small and tiny *grumeaux*. In that case, goethite does not replace kaolinite but "coexists with it."

3. In seasonally varying tropical soils, goethite predominates only in downslope profiles (wet, most of the time) in the mottle zones, where the water table fluctuates and in saprolites and lithomarges below the water table. Here again, goethite and kaolinite coexist with no replacement of the clay by the oxihydroxide.

4. Goethites of these types are all more or less aluminous and may contain up to 30 mole percent diaspore. The aluminum content is controlled by the aluminum available in solution in which goethites form. As shown for example by Fritz and Tardy (1974, 1976) or Fritz (1981), aluminum in solution increases during a mineral sequence, as one goes from montmorillonite to kaolinite plus quartz, then to kaolinite without quartz, and finally to gibbsite. From dry to humid climates, from downslopes to upslopes, from bottom to the top of the profiles, drainage and leaching increase, silica concentrations in solutions decrease, while aluminum in solution and in goethite increase together. The aluminum content of goethites coexisting with kaolinite is controlled by the silica activity in solution, probably much more than by other factors that accompany the leaching such as pH, organic matter content, *et cetera*.

5. Hematite appears at the top of some old bauxitic profiles, together with boehmite and sometimes with diaspore. Generally, hematite is not abundant when gibbsite dominates.

6. Therefore, under seasonally varying tropical climates, in the upper parts of the upslope profiles above the mottled zones, in concretioned horizons, hematite appears as a very common mineral. Then, the formation of hematite in concretions follows the formation of goethite in mottles.

7. When a concretion develops, iron is enriched in zones of small size porosity, in preference to the areas in which large sized pores pre-

dominate. This is the reason hematite forms predominantly in microenvironments in which kaolinite was initially abundant. Therefore, instead of merely coexisting, as observed for goethite, hematite replaces kaolinite and becomes aluminous. The reason for this replacement is essentially the instability of kaolinite in the unsaturated zone. Furthermore, the hematite is extremely finely crystallized.

8. In the upper parts of ferricretes, dismantling takes place, and large channels develop. Along the margins of the oxide concretions and in contact with large size pores periodically visited by percolating waters, aluminous hematites alter into secondary aluminum-rich goethites. These secondary minerals are transformed, in turn, into less and less aluminous goethites, relatively better crystallized than the replaced hematites.

9. At sufficiently high activities of water and at sufficiently low activities of silica in solution, gibbsite forms together with Al–goethite. The aluminum content in goethite is fixed, when the activity of water is fixed. If the water activity diminishes or if the activity of silica increases if the ratio of Al/Fe diminishes, gibbsite does not form. Thus, the stability field of gibbsite is limited by either boehmite, kaolinite, or Al–goethite formation. Hematite forms when the activity of water and the ratio Al/Fe are both low. When Al–hematite or Al–goethite form alone, their aluminum content is determined by the composition of the system; when they form together, their compositions are determined only by the activity of water. In this case, the amount of each mineral is then determined by the activity of water and by the Al/Fe ratio in the system.

10. Finally, the parameters that control the relative stability of hematites and goethites are: (1) grain size of particles, (2) aluminum, iron, and water content in the system, (3) activity of silica when kaolinite or smectite is present, (4) activity of water, that is, saturated or non-saturated regime and in the latter case pore size in which minerals form.

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