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Stability fields of clays and aluminum phosphates: parageneses in lateritic weathering of argillaceous phosphatic sediments

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Abstract

Several methods of estimating thermodynamic data of natural phosphates were unable to predict with enough accuracy stability fields of such minerals and the parageneses observed in natural conditions. Detailed observations made on lateritic weathering profiles, from the bottom to the top, yield the following mineral associations:

Fluor-carbonate-apatite + montmorillonite + calcite → fluor-carbonate-apatite + montmorillonite → fluor-carbonate-apatite + kaolinite → crandallite + kaolinite → wavellite + kaolinite → augelite → gibbsite.

A refined method for estimating Gibbs free energies of formation of these phosphates is proposed. A first step of estimation is based on the summation of the Gibbs free energies of formation of simple components and an additional term which depends on the nature of cations in each compound. A second calibration step is based on the correction of the additional term so that the Gibbs free energies of formation and the fields of stability of the phosphates and clay minerals would be in good agreement with the natural observed sequence. These estimations yield the following values (kcal/mole):

Fluor-carbonate-apatite, $Ca_{10}(PO_4)_5CO_3F_3$: $\Delta G^\circ_f = -2983.3$
Crandallite, $CaAl_3(PO_4)_2(OH)_5 \cdot H_2O$: $\Delta G^\circ_f = -1336.7$
Wavellite, $Al_3(PO_4)_2(OH)_3(H_2O)_4 \cdot H_2O$: $\Delta G^\circ_f = -1330.0$
Augelite, $Al_2PO_4(OH)_3$ $\Delta G^\circ_f = -660.9$
Variscite, $Al_2PO_4 \cdot 2H_2O$: $\Delta G^\circ_f = -498.8$
Ca-millisite, $Ca_{1.5}Al_6(PO_4)_4(OH)_9 \cdot 3H_2O$: $\Delta G^\circ_f = -2614.0$

Introduction

The phosphate plateau of Thies in Senegal yields an almost complete sequence of clays and calcium–aluminum–hydroxy–phosphates, commonly found in lateritic weathering profiles: fluor-carbonate-apatite, calcite, montmorillonite, kaolinite, millisite, crandallite, and wavellite. Some profiles in other regions yield also millisite, variscite, augelite and gibbsite (Flicoteaux *et al.*, 1977). A recent method proposed by Nriagu (1976) for estimating Gibbs free energies of formation of phosphates has been applied to the determination of the stability fields of these minerals, but has shown a large discrepancy between the calculated and the observed data. For example, Nriagu's values determine a field of stability of crandallite and wavellite too large with regard to the stability fields of montmorillonite and kaolinite; in these conditions, clay minerals should not exist in natural parageneses. An attempt to refine such estimated data by examining their coherence with field observations is now presented.

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Rough estimation of Gibbs free energies of formation of apatites and calcium–aluminum–hydroxy–phosphates

Vieillard (1978) compiled the different values of Gibbs free energy, enthalpy, and entropy of formation of phosphates available in the literature. Most of the thermodynamic data are from measurements, but some are simply estimated. Different methods of estimating enthalpies and Gibbs free energies of formation, based on the corresponding-state relationship principle, have been presented for relatively simple minerals such as meta-, ortho-, and pyrophosphates. Recently, Nriagu (1976) and Nriagu and Dell (1974) proposed a method, roughly similar to that of Tardy and Garrels (1974), for naturally-occuring hydroxy-phosphates. This method is based upon the summation of the free energies of formation of simple components. The Gibbs free energy for a given hydroxy-phosphate is equal to the sum of three terms: ΔG°_f hydroxy-phosphate $= \Sigma_i \Delta G^\circ_f(r_i) + x\Delta G^\circ_f\ \text{H}_2\text{O} - Q$, in which $\Sigma_i \Delta G^\circ_f(r_i)$ is the sum of the Gibbs free energies of the hydroxides or simple phosphates forming the hydroxy-phosphates, x is the number of moles of water involved in the complex phosphate, and $Q = 2.303RT\,\Sigma n_i \log n_i$, where n_i is the stoichiometric coefficient of the i^{th} hydroxide or the simple phosphate. This method yields a difference between the predicted and experimental results generally better than ±5 percent; however, it appears that this difference is too large for interpretations of natural parageneses.

Vieillard (1978) used Nriagu's method of estimation but modified the expression of the term Q according to the new data obtained by Tardy and Garrels (1976, 1977), Tardy and Gartner (1977), and Tardy and Vieillard (1977). Then, incorporating this modification, the Gibbs free energy of formation of a given compound [$\text{Ca}_3(\text{PO}_4)_2$ as an example] formed of two oxides is equal to

$$\Delta G^\circ_f\ \text{Ca}_3(\text{PO}_4)_2 = 3\Delta G^\circ_f\text{CaO} + \Delta G^\circ_f\text{P}_2\text{O}_5 - \alpha\,\frac{n_1 \times n_2}{n_1 + n_2}\,(\Delta\text{O}^{2-}\text{Ca} - \Delta\text{O}^{2-}\text{P}) \qquad (1)$$

In this equation α is a coefficient characterizing the same family of compounds (phosphates, carbonates, *etc.*); n_1 and n_2 are, respectively, the number of oxygen bounded with each of the cations ($n_1 = 3$ for CaO, $n_2 = 5$ for P_2O_5); ΔO^{2-} Ca and ΔO^{2-} are parameters characterizing the cations (ΔO^{2-} cation is equal to the difference between the Gibbs free energies of formation of the oxide and the aqueous cation).

This concept has been extended by Vieillard (1978) to more complex compounds such as monetite (CaHPO_4). For example:

$$\Delta G^\circ_f\text{CaHPO}_4 = \frac{1}{3}\,\Delta G^\circ_f\text{Ca}_3(\text{PO}_4)_2 + \frac{1}{3}\,\Delta G^\circ_f\text{H}_3\text{PO}_4 - \alpha'\,\frac{\frac{8}{3}\times\frac{4}{3}}{4}\,[\text{mean }\Delta\text{O}^{2-}\text{Ca}_3(\text{PO}_4)_2 - \text{mean }\Delta\text{O}^{2-}\ \text{H}_3\text{PO}_4] \qquad (2)$$

Coefficients $\frac{8}{3}$ and $\frac{4}{3}$ are, respectively, the number of oxygen bounded with each of the two compounds [$\frac{8}{3}$for$\frac{1}{3}\text{Ca}_3(\text{PO}_4)_2$, $\frac{4}{3}$ for$\frac{1}{3}\text{H}_3\text{PO}_4$]; α' is a specific coefficient for neutral and acid phosphates formed by three components; mean $\Delta\text{O}^{2-}\text{Ca}_3(\text{PO}_4)_2$ and mean ΔO^{2-} H_3PO_4 refer respectively to the weighted average of the ΔO^{2-} cation constituting the simple compounds $\text{Ca}_3(\text{PO}_4)_2$ and H_3PO_4, as for example:

$$\text{mean }\Delta\text{O}^{2-}\text{Ca}_3(\text{PO}_4)_2 = \frac{3\Delta\text{O}^{2-}\text{Ca} + 5\Delta\text{O}^{2-}\text{P}}{8}$$

$$\text{mean }\Delta\text{O}^{2-}\text{H}_3\text{PO}_4 = \frac{1.5\Delta\text{O}^{2-}\text{H} + 2.5\Delta\text{O}^{2-}\text{P}}{4}$$

For all complex orthophosphates with three cations $\alpha' = 0.335$. The difference between the measured and the calculated free energy is statistically equal to ±2.5 kcal/mole.

For the estimation of the Gibbs free energy of formation of basic phosphates such as $\text{Al}_2\text{PO}_4(\text{OH})_3$, an equation similar to equation (2) was used:

$$\Delta G^\circ_f\text{Al}_2\text{PO}_4(\text{OH})_3 = \Delta G^\circ_f\text{AlPO}_4 + \Delta G^\circ_f\text{Al(OH)}_3 - \beta \times \frac{4\times 3}{7}\,[\text{mean }\Delta\text{O}^{2-}\text{Al(OH)}_3 - \text{mean }\Delta\text{O}^{2-}\ \text{AlPO}_4] \qquad (3)$$

β is a coefficient analogous to α'. From experimental data for augelite [$\Delta G^\circ_f\text{Al}_2\text{PO}_4(\text{OH})_3 = -671.5$ kcal/mole (Wise and Loh, 1976)] one obtains $\beta = 0.77$. The estimated value given by Nriagu (1976) [$\Delta G^\circ_f\text{Al}_2\text{PO}_4(\text{OH})_3 = -665.3$ kcal/mole] yields $\beta = 0.45$.

By using alternatively one of these two values for β, Vieillard (1978) estimated the free energies of formation of several phosphates (Table 1) such as wavellite and crandallite. These minerals can be considered as hydroxy-phosphates after removal of H_2O. The Gibbs free energy contribution of H_2O was estimated from the values of hydration of $\text{AlPO}_4\cdot 2\text{H}_2\text{O}$ or

$CaSO_4 \cdot 2H_2O$ and fixed at −56.7 kcal/mole for zeolitic water and −57.0 kcal/mole for ligand water.

Table 1 shows a considerable discrepancy among data from different sources. Further investigations based upon natural observations necessitate a drastic revision of the values of the coefficient β. The value which corresponds to the observations must be close to 0.30 instead of 0.45 calculated from Nriagu (1976) and 0.77 from Wise and Loh (1976).

Table 1. Gibbs free energies of formation of several phosphates from different sources

Mineral names and formulae	ΔG_f° Measured	ΔG_f° Estimated (Nriagu, 1976)	ΔG_f° Calculated † (Vieillard, 1978)		
			$\beta=0.77$	$\beta=0.45$	$\beta=0.30$
Augelite $Al_2PO_4(OH)$	-671.50(1)	-665.30	-671.50	-665.30	-662.11
Wavellite $Al_3(PO_4)_2(OH)_3(H_2O)_4.H_2O$	-	-1339.	-1343.20	-1335.00	-1331.15
Crandallite $CaAl_3(PO_4)_2(OH)_5(H_2O)$	-	-1342.	-1364.02	-1345.50	-1336.61
Calcic millisite $Ca_{1.5}Al_6(PO_4)_4(OH)_9 \cdot 3H_2O$	-	-	-	-	-2613.22
Variscite $AlPO_4(H_2O)_2$	-503 (2)	-498.8 (3)			

References : (1) - Wise and Loh (1976) ; (2) - Lindsay, Peech and Clark (1959) ; (3) - This study.

† ΔG_f° of minerals based on (kcal/mole) :

ΔG_f° $AlPO_4$ = −382.70
ΔG_f° $Al(OH)_3$ = −273.35
ΔG_f° $Ca(OH)_2$ = −214.76
ΔG_f° H_2O (lig.) = −57.00
ΔG_f° H_2O (zeol.) = −56.69
ΔO^{2-} Al^{3+} = −48.73
ΔO^{2-} H^+ = −53.00
ΔO^{2-} Ca^{2+} = −12.07
ΔO^{2-} P^{5+} = −71.00

Parageneses of lateritic weathering on phosphatic sediments

Lateritic weathering of alternate layers of calcareous phosphates and argillaceous sediments, transformed into aluminous phosphates, are found in Senegal (Capdecomme, 1952, 1953; Slansky *et al.*, 1964); in Nigeria (Russ and Andrews, 1924); in Florida (Espenshade and Spencer, 1963, and others); in Siberia (Zanin, 1968); and on Christmas Island (Trueman, 1965). Recent studies of Flicoteaux *et al.* (1977) on the Eocene–Oligocene argillaceous and phosphatic deposits of Lam-Lam (Thies Plateau in Senegal) have shown vertical and lateral relationships during mineral parageneses. Weathering profiles yield a succession of horizons or layers, which from bottom to top are (Fig. 1):

(a) *Parent rocks* composed of alternating (1) argillaceous or argillaceous silty layers with montmorillonite (80 percent) + illite (10 percent) or rarely attapulgite (70 percent) + montmorillonite (30 percent), with a small amount of phosphate; (2) calcium phosphate layers with carbonate-fluorapatite and a dispersed clay mineral fraction composed of montmorillonite + illite.

(b) *A transition horizon* which shows a progressive upward transformation of parent-rock minerals. (1) In the argillaceous or argillaceous silty layers, kaolinite rapidly forms from the montmorillonite and reaches 90 to 100 percent of the clay mineral fraction. Illite is present in the amount of 0 to 10 percent. The carbonate-fluorapatite fraction is transformed into millisite which forms small spherical crystal aggregates. This horizon is initially gray, but becomes red or ochrous owing to the formation of goethite. (2) In the calcium phosphate layers the porosity increases. The clay mineral fraction rapidly becomes kaolinitic. In the lower transition horizon the layers are still composed of carbonate-fluorapatite with a few millisite spheres. Upwards, the millisite spheres become more numerous, and crandallite appears and spreads out. The millisite–crandallite association constitutes a widely-developed crystalliplasma (in the sense of Brewer, 1964, p. 317). All these transformations are achieved with conservation of original volumes and sedimentary features.

(c) *Gray and ochrous calcium–aluminum–phosphate horizon.* In the argillaceous or argillaceous silty layers, the quantity of kaolinite decreases and is replaced by a millisite + crandallite crystalliplasma. Crandallite is not very abundant at the base of this zone, but increases progressively and becomes the dominant mineral at the top. In the phosphate beds the same development of crandallite is observed: (1) radiating needles on the order of 1–3mm in the crystalliplasma *sensu stricto*; (2) short perpendicular needles at the edges of voids developing upwards. Detrital quartz, so far preserved, is marked by corrosion vugs or cracks cutting grains into several pieces. Under crossed polarizers simultaneous extinction can be seen in all pieces of an original quartz grain, which indicates dissolution *in situ*. The dissolution vugs are filled with crandallite crystalliplasma. Here again, original volumes are preserved in the horizon.

(d) *White aluminophosphate horizon.* Wavellite crystals first form on the edge of voids close to the needles of crandallite. Then these crystals begin to appear and become more numerous in the crandallite crystalliplasma itself. Progressively, needles of wavellite replace all the crandallite and spread out into the plasma. Quartz is completely dissolved, and kaolinite is present in very small amounts. In this horizon original sedimentary features and volumes are still conserved.

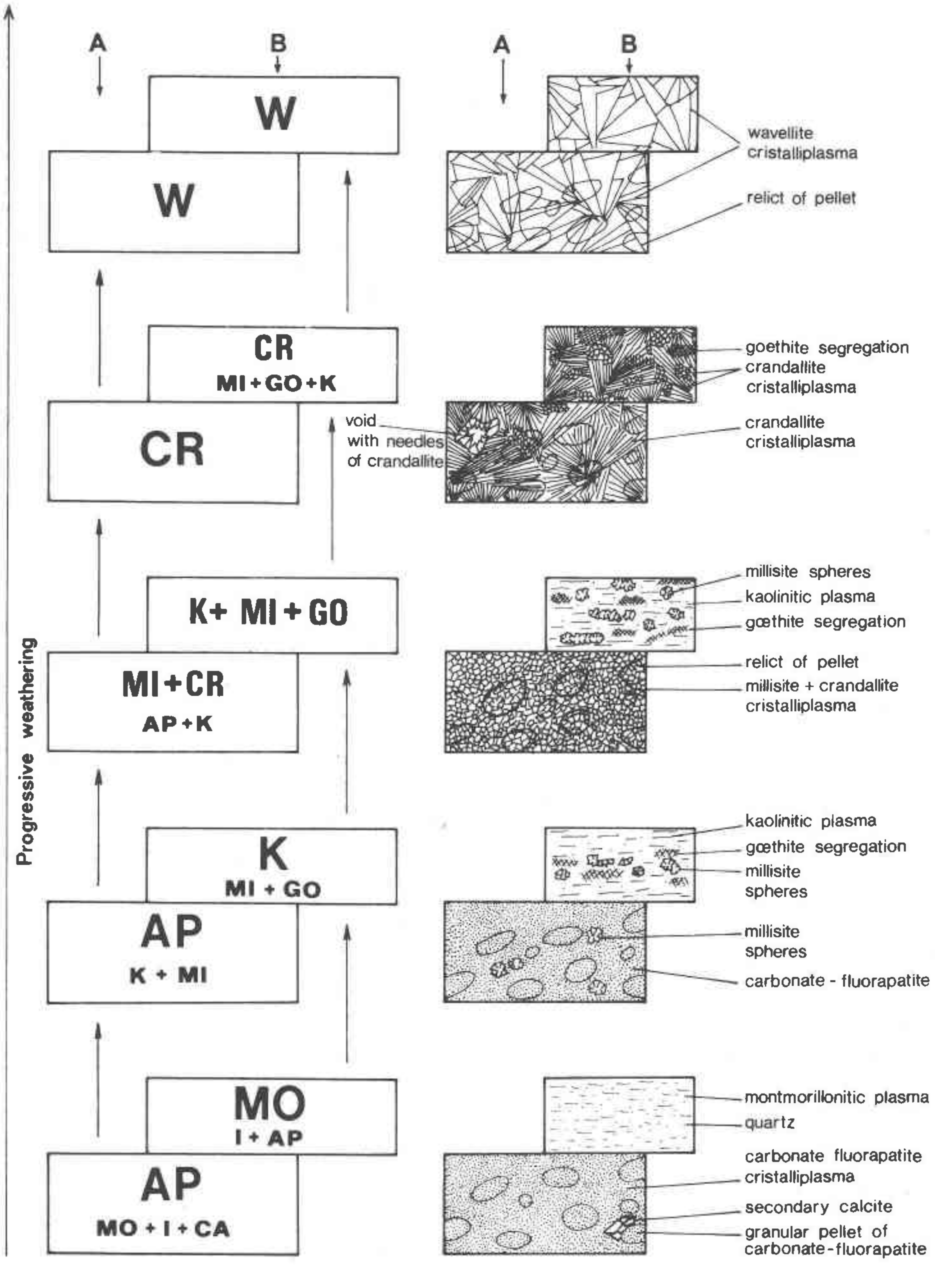

Fig. 1. Mineral paragenesis sequences in the Lam-Lam lateritic profiles (Thies plateau, Senegal). Column A refers to phosphatic beds; column B refers to argillaceous beds. Size of letters is roughly proportional to the abundance of minerals. MO = montmorillonite; I = illite; CA = calcite; AP = fluor-carbonate-apatite; K = kaolinite; MI = millisite; GO = goethite; CR = crandallite; W = wavellite.

(e) *Secondary minerals filling voids and cracks.* A system of voids and cracks of various size marks the different horizons. These voids, which cross sedimentary features and structures, are sometimes secondarily coated or filled by mineral accumulations. The nature of these secondary minerals changes within the profile: at the bottom, in the almost fresh apatite bedrock, sparry calcite crystal coats are observed; above, but always in the lower part of profiles, secondary apatite, quartz and chalcedony are present; in the upper horizons, fillings or coatings, often red in color, are composed of kaolinite and goethite. Later, kaolinite is sometimes replaced partly or completely by millisite; kaolinite coatings are laterally transformed into millisite coatings.

All these secondary minerals (calcite, quartz +

Table 2. Chemical formulae, Gibbs free energies of formation, and solubility products of minerals used in the diagrams

Mineral name	Chemical formulae	ΔG°_f (kcal/mole)	Solubility product at 25°C		Réf.
Calcite	$CaCO_3$		$\log [Ca^{2+}] / [H^+]^2 + \log fCO_2 =$	9.76	(1)
Montmorillonite-Ca	$[Si_{3.67}Al_{0.33}]\,Al_2O_{10}(OH)_2Ca_{0.167}$	− 1279.24	$\log [Ca^{2+}] / [H^+]^2 + 14 \log [Al^{3+}] / [H^+]^3 + 22 \log [H_4SiO_4]$	37.10	(1)
Kaolinite	$Al_2Si_2O_5(OH)_4$	− 907.68	$2 \log [Al^{3+}] / [H^+]^3 + 2 \log [H_4SiO_4] =$	7.63	(1)
Gibbsite	$Al(OH)_3$	− 274.88	$\log [Al^{3+}] / [H^+]^3 =$	8.24	(2)
Apatite	$Ca_{10}(PO_4)_5(CO_3)F_3$	− 2983.3	$8{,}5 \log [Ca^{2+}] / [H^+]^2 + 1{,}5 \log [Ca^{2+}] + 3 \log [F^-]$ $+ 5 \log [H_3PO_4] + \log f\,CO_2 =$	41.06	(3)
Crandallite	$CaAl_3(PO_4)_2(OH)_5(H_2O)$	− 1336.7	$\log [Ca^{2+}]/[H^+]^2 + 3 \log [Al^{3+}] / [H^+]^3 + 2 \log [H_3PO_4]$	21.95	(3)
Wavellite	$Al_3(PO_4)_2(OH)_3(H_2O)_4 \cdot H_2O$	− 1330.0	$3 \log [Al^{3+}] / [H^+]^3 + 2 \log [H_3PO_4] =$	12.95	(3)
Augelite	$Al_2PO_4(OH)_3$	− 660.9	$2 \log [Al^{3+}] / [H^+]^3 + \log [H_3PO_4] =$	10.47	(3)
Variscite	$AlPO_4 \cdot (H_2O)_2$	− 498.8	$\log [Al^{3+}] / [H^+]^3 + \log [H_3PO_4] =$	2.67	(4)
Calcic-Millisite	$Ca_{1.5}Al_6(PO_4)_4(OH)_9 \cdot 3H_2O$	− 2614.0	$1{,}5 \log [Ca^{2+}] / [H^+]^2 + 6 \log [Al^{3+}] / [H^+]^3$ $+ 4 \log [H_3PO_4] =$	38.90	(4)
Fluorite	CaF_2	− 279.0	$\log [Ca^{2+}] + 2 \log [F^-] =$	− 10.00	(3)

References : (1) - Helgeson (1969) ; (2) - Fritz and Tardy (1973) ; (3) - Vieillard (1978) ; (4) - This study.

* Solubility products are based on : ΔG°_f H_4SiO_4 (aq) = − 312.56 kcal/mole; ΔG°_f CO_2 (g) = − 94.254 kcal/mole

ΔG°_f Al^{3+} (aq) = − 116.0 kcal/mole; ΔG°_f F^- (aq) = − 66.64 kcal/mole

ΔG°_f Ca^{2+} (aq) = − 132.3 kcal/mole; ΔG°_f H_2O (liq) = − 56.69 kcal/mole

ΔG°_f H_3PO_4 (aq) = − 273.10 kcal/mole

chalcedony + apatite, kaolinite) are oriented perpendicularly to the edges of the voids. Thus, they are authigenic. These sequences of secondary minerals show: (1) the leaching of material from the horizons above, and (2) the order of accumulation in the profile: the most calcitic, the most soluble minerals are located lower and the most aluminous, *i.e.* the least soluble, are located higher in the profiles.

The lateritic profiles of Lam-Lam show that two sequences of weathering are present:

montmorillonite → kaolinite
carbonate-fluorapatite → millisite → crandallite → wavellite

Before the complete transformation of carbonate-fluorapatite, kaolinite is formed and secondary calcite is dissolved. In other lateritic profiles of Lam-Lam, millisite is occasionally absent, and augelite appears locally near the surface grading to wavellite (Capdecomme, 1952; Flicoteaux *et al.,* 1977). The succession is as follows:

carbonate-fluorapatite → crandallite →
wavellite → augelite

Visse (1952) described gibbsite in the Thies Plateau profiles. This indicates that under particular conditions, following kaolinite and aluminous phosphates, the ultimate term of the evolution can be reached. Furthermore, in the weathering of Eocene phosphatic sediments of the Eboïda area (Ivory Coast, near Ghana), millisite is missing and variscite occurs between crandallite and wavellite zones (Charpy and Nahon, 1978).

The sequence of mineral weathering presented in Figure 2 and Table 2 is: calcite, montmorillonite, apatite, kaolinite, crandallite, wavellite, augelite, and gibbsite. Calcium is the element most easily leached, first from carbonates, then from silicates, and finally from phosphates. Silica is removed rapidly as compared to phosphorus, which remains a long time in the profiles, thus delaying the formation of gibbsite. Iron, present in montmorillonite, appears as goethite and is not included in phosphates. This observed sequence can be used to refine the thermodynamic data and stability fields of calcium-aluminum phosphates and silicates.

Stability fields of apatite, millisite, crandallite, wavellite, variscite, and augelite

From the initial estimated values of ΔG°_f a first set of stability fields was drawn and then modified until it was in good accordance with sequences in the field. A three-dimensional diagram, using as axes log $[H_4SiO_4]$, log $[Ca^{2+}]/[H^+]^2$ and log $[H_3PO_4]$, was fi-

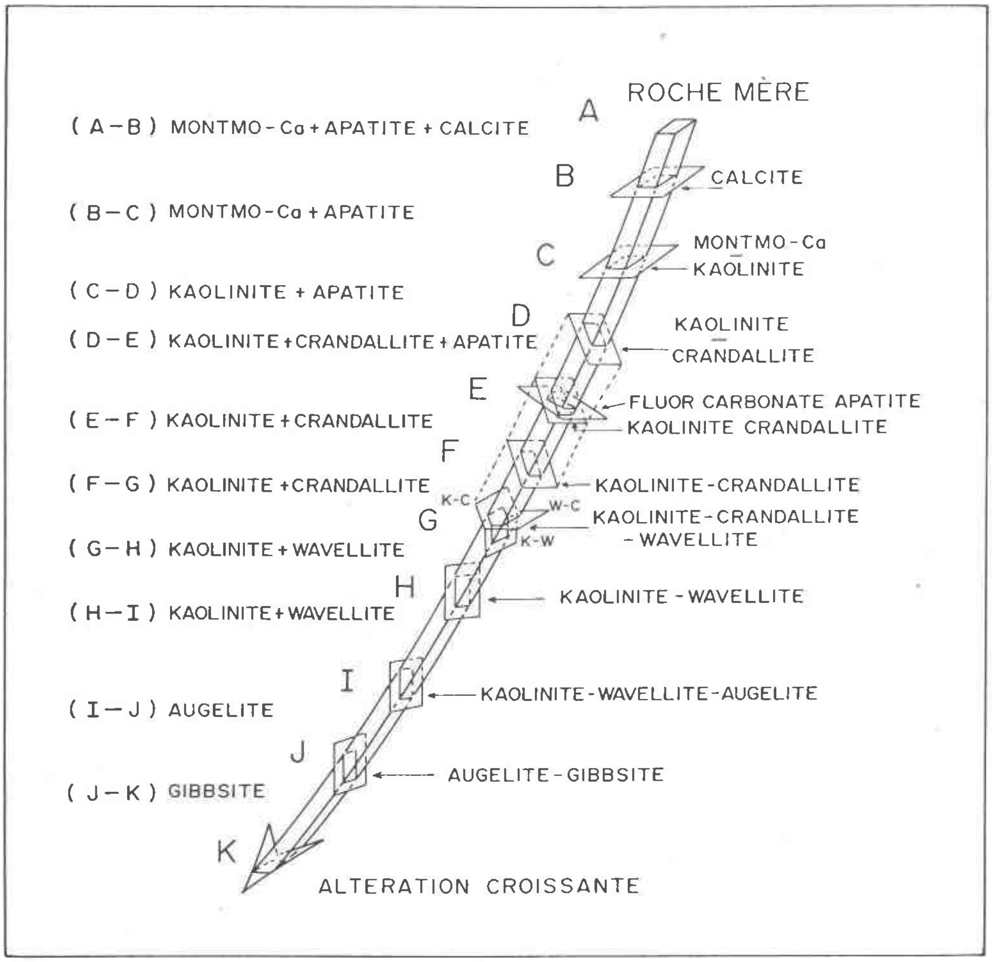

Fig. 2. Schematic chemical path of solutions during weathering of argillaceous phosphates. The sense of evolution is that of a progressive dilution of solutions from the base to the top of the profiles.

nally obtained (Fig. 3). A simulated chemical-weathering path from A to K is presented in Figure 2 and detailed in the two-dimensional diagrams of Figure 4. The path A–K illustrates the general chemical change of a solution initially in equilibrium with primary minerals in a parent rock, and then progressively diluted and continuously at saturation with respect to the successive secondary mineral associations. This evolution simulates a lateritic weathering profile, presented in a reverse sense to that of circulating solutions.

The associations encountered along the path are the ones described in the previous section and illustrated in Figure 1; the chemical compositions of the minerals represented by the stability fields are those of natural minerals, except apatite and montmorillonite, for which the formulas have been simplified. Natural fluor-carbonate-apatite is replaced by francolite [$Ca_{10}(PO_4)_5(CO_3)F_3$], and montmorillonite is considered as a pure calcium aluminum silicate. The solubility constants used for drawing the diagrams are given in Table 2.

The ΔG°_f values calculated for the alumino-hydroxy-phosphates from known solubility constants and from approximated constants based upon mineral parageneses were used to calculate a new value for the parameter β. This value is found to be close to 0.30 for the four minerals considered (calcic millisite, crandallite, wavellite, and augelite).

Several problems were encountered in calculating the stability fields of minerals in a two-dimensional diagram: log $[Ca^{2+}]/[H^+]^2$, log $[H_3PO_4]$. For the fluor-carbonate-apatite, the activity of $[F^-]$ was assumed to be limited by the fluorite precipitation [$2\log(F^-) + \log(Ca^{2+}) = -10$], and the fugacity of CO_2 is presumed to be such that $\log fCO_2 = -2.5$. The

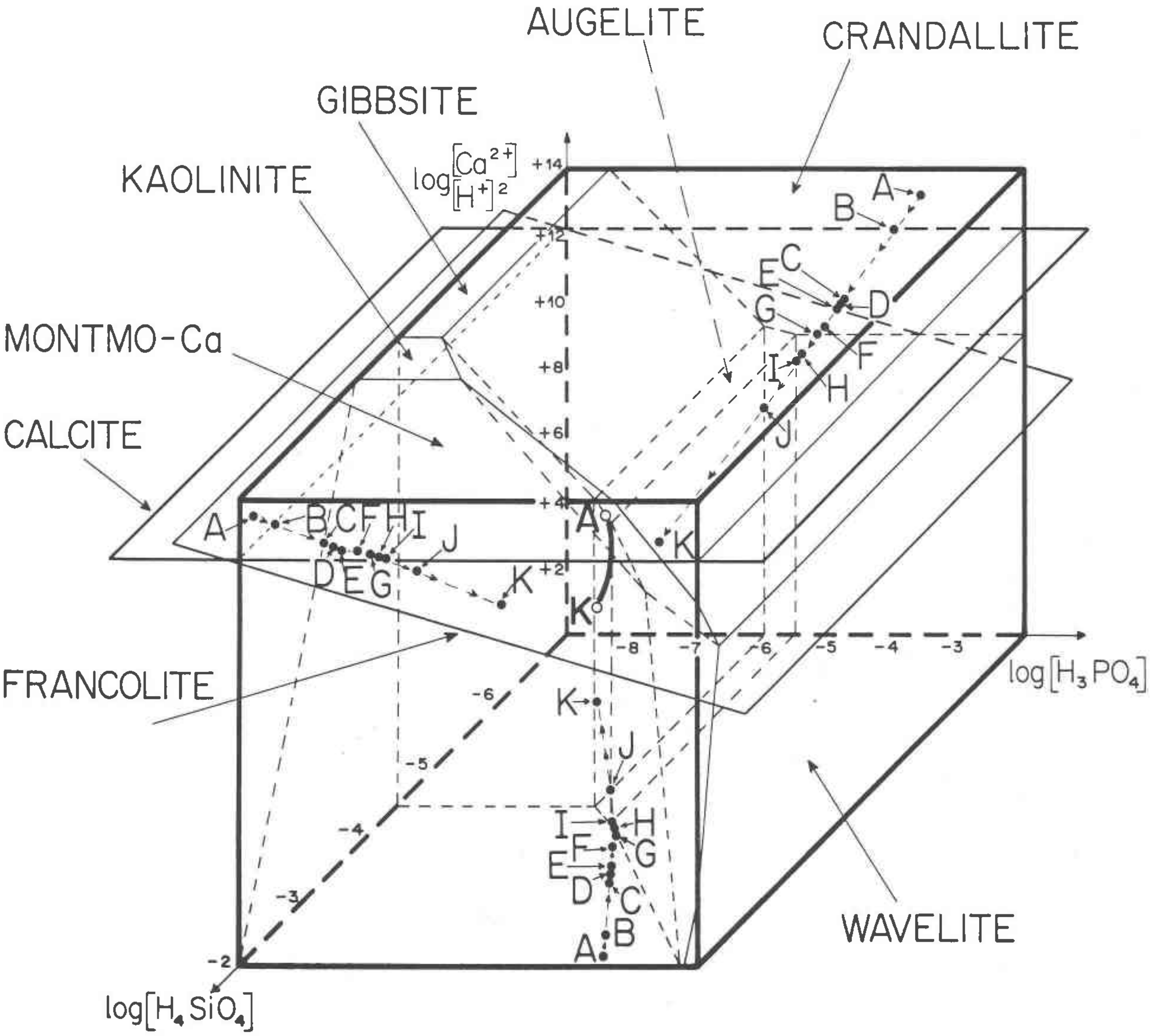

Fig. 3. Three-dimensional stability field diagram, for calcite, francolite, calcium aluminum silicates, and phosphates.

stability field of variscite is not represented in Figure 4 for simplification only. It appears between crandallite and wavellite. The stability field of Ca-millisite is not represented in Figure 4 because the value obtained in Table 2 does not fit this mineral stability between apatite and crandallite as observed in the field.

It should be remembered that, although in nature millisite appears between apatite and crandallite, this mineral is not entirely calcic but contains a significant quantity of sodium [$Ca_{1.25}Na_{0.5}Al_6(PO_4)_4(OH)_9 \cdot 3H_2O$], according to published analyses. In conclusion, it can be supposed that, in natural conditions, (1) millisite is formed only because of the incorporation of sodium, and (2) pure calcic millisite is unstable relative to crandallite.

Discussion

The method followed in this work utilizes two different approaches to determine the values for Gibbs free energy, *i.e.* estimation of thermodynamic data on one hand and feedback control from natural observations on the other. The second method is in fact based on the assumptions of internal consistency among stability fields of silicates such as montmorillonite, kaolinite, and gibbsite and phosphates such as francolite, millisite, crandallite, variscite, wavellite, and augelite.

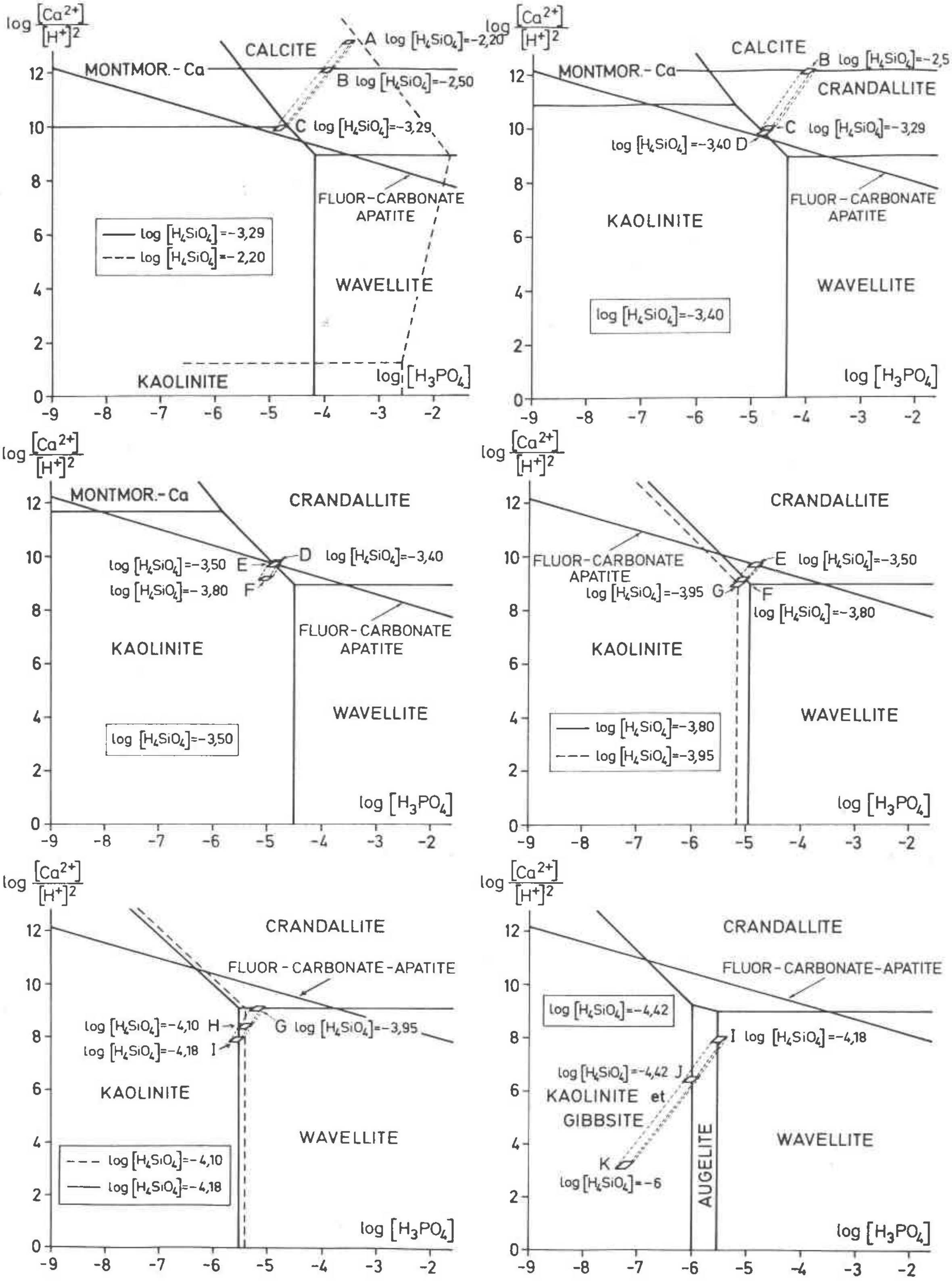

Fig. 4. Two-dimensional activity diagrams (log $[Ca^{2+}]/[H^+]^2$, log $[H_3PO_4]$) for different values of log $[H_4SiO_4]$.

Clearly, in lateritic profiles, the presence of phosphate in the bedrock alters the usual geochemical behavior of calcium, silicon, aluminum, and iron observed in the weathering of pure silicate rocks under same climatic settings. Calcium is quickly leached from silicate-derived profiles but is retained longer in phosphate formations. Kaolinite is dominant in profiles with silicate parent rocks but becomes ephemeral in a phosphatic weathering sequence. Finally, gibbsite, a frequent weathering product on crystalline silicate rocks under humid tropical conditions, is rare in weathering of phosphatic deposits. The presence of low-solubility aluminum phosphates keeps the mole fraction of diaspore within the aluminum-rich goethite extremely low until the aluminum phosphates are destroyed. Only then does goethite reach the value of 15–25 percent mole fraction of diaspore, usually present in iron crust (ferricretes). Such observations illustrate the geochemical role of phosphate in lateritic weathering.

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