

## QUARTZ PRESENCE IN RELATIONSHIP TO GIBBSITE STABILITY IN SOME HIGHLY WEATHERED SOILS OF BRAZIL\*

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**Abstract**—Determination of the mineralogical composition of six highly weathered soils of the Central Plateau of Brazil showed that the sand content (predominantly quartz) was not related to the relative amounts of gibbsite and kaolinite in the clay (<2 μm) fractions. The latter is in agreement with kinetic considerations of the involved mineral species, but in disagreement with thermodynamic considerations. However, that dissolution of quartz has been operative in these soils is indicated by an excellent relationship ( $r^2 = 0.96$ ) between the amount of sand-size quartz and the reactive SiO<sub>2</sub> content of the clay fractions.

### INTRODUCTION

Quartz is commonly the predominant primary mineral occurring in the sand size fraction of highly weathered soils of humid tropical regions. Its persistence in these soils is attributed to its extreme chemical inertness. Accordingly, quartz presence is generally thought to have little influence on, or relationship to, the nature of the secondary minerals present in highly weathered soils which are usually oxides of iron and aluminum, and kaolinite. Nevertheless, it has been suggested (Gardner, 1970; Curtis, 1970) that quartz presence in soils may prevent the formation and/or stability of gibbsite. The latter conclusion was based on considerations of the solute activities of H<sup>+</sup>, Al<sup>3+</sup> and Si(OH)<sub>4</sub> corresponding to the thermodynamic stability of kaolinite, gibbsite and quartz as given in Fig. 1. (The thermodynamic values used in the construction of this diagram are those given by Kittrick (1969) for well crystallized gibbsite and kaolinite.) Essentially, the diagram shows that under weathering conditions of acid pH and where Al is not limiting, as is usually the case in environments and landscapes conducive to the formation of highly weathered soils, gibbsite will be stable relative to kaolinite only when the activity of Si(OH)<sub>4</sub> is extremely low (less than  $p\text{Si(OH)}_4 = 4.8$ ). The diagram also shows that soils, in which gibbsite and kaolinite thermodynamically co-exist, should have solute activities corresponding to the intersection of the gibbsite and kaolinite stability lines at  $p\text{Si(OH)}_4 = 4.8$  and  $\text{pH} - 1/3p\text{Al} = 2.7$ . The position of the stability line for quartz ( $p\text{Si(OH)}_4 = 3.74$ ; Siever, 1962) indicates that quartz presence should cause Si(OH)<sub>4</sub> activities greater than that associated with gibbsite-kaolinite equilibrium. Hence, in

the presence of quartz, gibbsite would be unstable relative to kaolinite. However, kinetic considerations may assume the significant role in this situation. As discussed by Kittrick (1969), the kinetics of quartz dissolution and precipitation are extremely slow at earth-surface temperatures and pressures and thus quartz may have less influence on gibbsite-kaolinite equilibrium than what might be expected from thermodynamic consideration.

Indeed, it is the extremely slow kinetics of quartz dissolution that causes laboratory studies to be unsuitable for investigation of this problem. Examination of actual occurrences of the involved mineral species in appropriate soil environments may prove

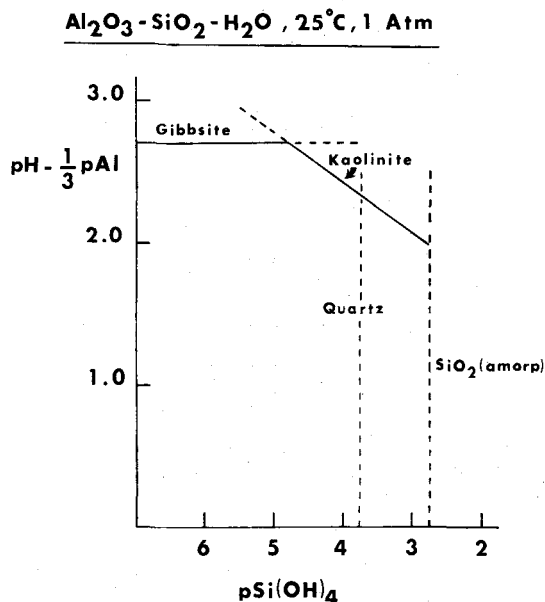


Fig. 1. Mineral stability diagram for gibbsite, kaolinite, and quartz in aqueous system of 25°C and one atmosphere as functions of  $p\text{Si(OH)}_4$  and  $\text{pH} - 1/3p\text{Al}$ .

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to be more advantageous. It was the purpose of this research to examine the mineralogical composition of some highly weathered soils from the Central Plateau of Brazil to determine whether or not the sand content (predominantly quartz) had any relationship to the nature of the clay mineral composition of the soils.

#### MATERIALS AND METHODS

The six soils examined in this study were taken from an area that is within the mid-portion of the Brazilian Central Plateau (Fig. 2). The present day climate of the area is characterized by a tropical seasonal regime of rainy summers and dry winters with a total annual rainfall of 2000 mm (FAO-UNESCO, 1971). The country rocks underlying the soils in the area are Devonian sandstones and Precambrian metamorphic rocks, including schists, phyllites and quartzite. The collected samples are representative of the soils that are found on first and second erosional surfaces in this area in which the land forms are classic examples of the result of multiple geomorphic cycles as discussed by Cline and Buol (1973). On these surfaces there are four general groups of soils that can be distinguished on the basis of color (Dark Red vs Red Yellow) and texture (loamy vs clayey). In the



Fig. 2. Location of sampling area.

Brazilian soil classification system, the soils would be classified as Dark Red and Red Yellow Latosols. In the U.S. Soil Taxonomy, the soils would be loamy or clayey textural varieties of Ustox (order—Oxisol; suborder—Ustic).

For purposes of characterization of the soils, the exchangeable cations Na, K, Ca and Mg were displaced by N  $\text{NH}_4\text{OAc}$  extraction and determined with an atomic absorption spectrophotometer; exchangeable aluminum was extracted by N KCl and measured colorimetrically by the aluminon procedure of McLean (1965); pH was determined in  $\text{H}_2\text{O}$  and N KCl at a 1:2 soil:solution ratio; and organic carbon by the Modified Walkley-Black method (Grewelling and Peech, 1965). For textural analyses, as well as for isolation of particle size fractions for mineralogical analyses, samples of the soils were treated with sodium hypochlorite ( $\text{NaOCl}$ ) of pH 9.5 (Anderson, 1963) for the destruction of organic matter and then separated into sand, silt, and clay fractions by wet sieving, centrifugation, and decantation (Jackson, 1969).

For X-ray diffraction (XRD) analyses, K- and Mg-saturated samples of the clay fractions were parallel-orientated onto glass slides and X-rayed with  $\text{CuK}\alpha$  radiation (35 kV, 15 mA) on a Norelco diffractometer fitted with a focusing monochromator and scintillation detector. Additional XRD patterns were obtained on the Mg-saturated samples following solvation with ethylene glycol and on the K-saturated samples after heating at 350 and 550°C. Random powder XRD patterns were determined on Mg-saturated samples of the sand and silt fractions.

Differential thermal analysis (DTA) was carried out on Ca-saturated clay samples diluted with ignited  $\text{Al}_2\text{O}_3$ . The analyses were obtained with an R. L. Stone DTA apparatus at a heating rate of 10°C/min with ignited  $\text{Al}_2\text{O}_3$  as the thermally inert reference material.

The free iron and aluminum oxide content of the soil clay fractions was determined by citrate-bicarbonate-dithionite (CBD) extraction (Jackson, 1969). Gibbsite and kaolinite contents were estimated by comparison of the DTA endothermic peak areas with those of reference gibbsite and kaolinite specimens. Mica was estimated from the  $\text{K}_2\text{O}$  content as given by  $\text{HF-H}_2\text{SO}_4$  digestion (1%  $\text{K}_2\text{O}$  = 10% mica). The  $\text{TiO}_2$  content was determined on the same digest by the colorimetric Tiron procedure as described by Dolcater *et al.* (1970). Amorphous or non-crystalline aluminosilicates were measured by the boiling 0.5 N NaOH procedure of Hashimoto and Jackson (1960). The latter was carried out on CBD-treated samples as preliminary studies indicated that prior removal of free iron oxides increased by up to 20%, the amount of extractable non-crystalline  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ . The more reactive or accessible non-crystalline aluminosilicates were extracted from the clay fractions by the dilute acid procedure (0.5 M  $\text{CaCl}_2$ , pH 1.5) of Tweneboah *et al.* (1967).

Table 1. Chemical and physical properties of soils

Profile and Sample No.	Depth (cm.)	pH		Carbon (%)	Exchangeable		Particle size distribution (%)		
		H <sub>2</sub> O	KCl		Bases (m-equiv. 100g <sup>-1</sup> )	Al (100g <sup>-1</sup> )	Sand (2-0.05mm)	Silt (2-50µm)	Clay (<2µm)
<b>Dark Red Latosol</b>									
I 2	0-20	5.2	4.3	2.19	0.26	0.59	21	10	69
3	40-60	5.4	4.5	1.47	0.09	0.34	20	15	65
4	100-120	6.0	4.9	0.83	0.06	0.06	26	17	57
<b>Dark Red Latosol</b>									
II 5	0-20	4.9	4.2	0.60	0.14	0.44	81	3	16
6	40-60	5.0	4.3	0.43	0.11	0.34	78	3	19
7	100-120	5.4	4.6	0.29	0.08	0.17	76	3	21
<b>Dark Red Latosol</b>									
III 8	0-20	5.4	4.6	1.50	0.55	0.17	65	6	29
9	40-60	5.3	4.9	0.92	0.15	0.04	63	14	23
10	100-120	6.1	5.6	0.63	0.11	-	63	16	21
<b>Red Yellow Latosol</b>									
IV 11	0-20	4.9	4.3	1.94	0.14	0.55	12	20	68
12	40-60	5.1	4.4	1.15	0.09	0.10	18	22	60
13	100-120	5.3	4.7	0.87	0.06	-	17	15	68
<b>Red Yellow Latosol</b>									
V 14	0-20	4.9	4.4	3.35	0.26	0.23	12	32	56
15	40-60	5.6	4.7	1.89	0.10	0.04	23	31	46
16	100-120	6.3	5.5	1.18	0.08	-	31	21	48
<b>Red Yellow Latosol</b>									
VI 17	0-20	5.0	4.2	1.24	0.12	0.41	60	9	31
18	40-60	4.9	4.3	0.74	0.07	0.07	54	12	34
19	100-120	5.6	5.0	0.37	0.05	-	55	16	29

## RESULTS AND DISCUSSION

*Soil chemical and physical properties*

The low amounts of exchangeable bases and relatively large amounts of exchangeable aluminum underscore the highly weathered nature of these soils (Table 1). A large proportion of the exchange capacity of these soils probably is associated with the organic matter as the exchangeable bases and exchangeable Al decreased markedly with depth as did the organic carbon content. The textural variation among the soils was considerable and this is probably a reflection of the relative amount of quartz present in the parent materials rather than differences in duration or intensity of weathering processes. Random powder XRD results confirmed that the sand and the silt fractions consisted predominantly of quartz with smaller amounts of TiO<sub>2</sub> minerals (rutile and anatase). In some of the silt fractions, small amounts of gibbsite and kaolinite were detected which were probably clay sized materials aggregated into silt size particles.

*Mineralogical analyses*

XRD results (Fig. 3) showed that kaolinite (7.2, 3.57 Å) and gibbsite (4.85, 4.37 Å) are predominant constituents of the soil clay fractions along with the iron oxides goethite (4.18, 2.69 Å) and hematite (2.69, 2.51 Å). Small reflections at 14 and 10 Å were observed for some of the clay fractions and probably correspond to an intergradient chlorite-like clay mineral and mica, respectively. The presence of these clay minerals became more definite (Fig. 4) when XRD analyses were repeated on the clay fractions following the removal of iron oxides by CBD treatment and of amorphous materials and gibbsite by the boiling 0.5 N NaOH treatment of Hashimoto and Jackson (1960). For the particular soil clay shown in Fig.

4, the 14 Å reflection of the treated sample collapsed partially to 10 Å upon K-saturation and heating 550°C, which would imply the presence of vermiculite with some Al-hydroxy interlayers. However, the apparent vermiculite content may be a treatment artifact as it has been shown (Dudas and Harward, 1970) that Al-hydroxy interlayers can be partially mobilized by a boiling 0.5 N NaOH treatment. XRD reflections for TiO<sub>2</sub> minerals—rutile (3.51 Å) and anatase (3.26 Å) also became more apparent after the dissolution treatments.

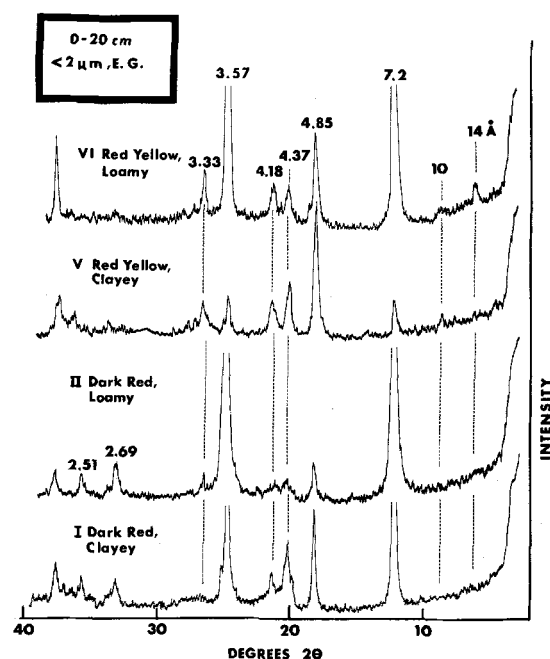


Fig. 3. X-ray diffraction patterns of the clay fractions of surface horizons (0-20 cm).

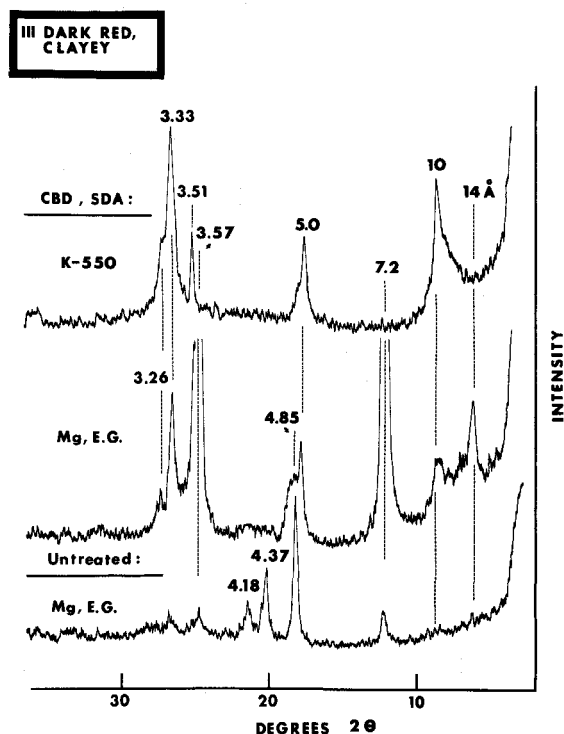


Fig. 4. X-ray diffraction patterns of Dark Red Latosol (111, 0–20 cm) clay fraction before and after CBD and 0.5 N NaOH treatment.

The quantitative estimates of the mineralogical composition of the clay fractions (Table 2) confirmed the XRD results. Appreciable quantities of mica were present in the clay fractions of soils V and VI, especially when it is considered that these highly weathered soils usually contain only traces of 2:1 layer silicates. The greater amounts of micaceous materials in soils V and VI are hardly attributable to a lesser degree of weathering as profile V which had the highest mica content also had the highest gibbsite content. Thus it seems likely that the parent

materials of soils V and VI had an higher initial content of dioctahedral mica of which at least a portion has persisted during soil development. Significant quantities of clay mica have also been reported in some Oxisols of South Africa (LeRoux, 1973). Its persistence was attributed to a peripheral chloritization (replacement of interlayer potassium by Al-hydroxy polymers) with a resultant stabilization of the residual mica cores. Presumably the same process has been operative in these Brazilian soils.

As has been noted in previous studies on highly weathered soils (LeRoux, 1973; Weaver, 1973) amorphous materials extracted by boiling 0.5 N NaOH constituted an appreciable portion of the clay fractions. The calculated  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratios (Table 3), after allocation of gibbsite  $\text{Al}_2\text{O}_3$ , ranged widely—0.80 to 6.0, but were generally within the range of 1.5 to 2.3 given by Jackson (1969) for siliceous amorphous materials characteristically found in highly weathered soils. The ratios, much in excess of the latter range, are most likely a consequence of the increased probability of experimental error when this procedure is applied to soil clay fractions containing large amounts of gibbsite.

The amounts of Si, Al, and Fe (Table 3) removed by the dilute acid extraction of Tweneboah *et al.* (1967) were extremely low and overall constituted not more than one per cent of the clay fractions. A comparison of the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios of the reactive components with those of the alkali-extractable amorphous materials (Table 3) shows that the reactive components differ from the latter by being relatively enriched in  $\text{Al}_2\text{O}_3$ . The complicated nature of non-crystalline materials that can be present in soils precludes precise analytical distinction, but these reactive components (Table 3) probably represent some fraction of the more accessible non-crystalline materials. It is possible that these reactive components are analogous to the permutite-like materials described by Jackson (p. 525, 1969).

Table 2. Mineralogical composition (%) of clay size fractions (<2  $\mu\text{m}$ )

Profile and Sample No.	Depth (cm)	CBD		Gibb	Kaol	Mica	Amorp	TiO <sub>2</sub>	Total
		Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>						
Dark Red Latosol									
I 2	0-20	8.0	2.3	27	36	1.6	20	2.1	97
3	40-60	8.6	1.8	26	44	nd	nd	nd	
4	100-120	8.1	2.1	27	44	0.2	22	2.1	106
II 5	0-20	17.9	2.2	9	40	0.8	23	5.7	99
6	40-60	16.8	2.4	9	34	nd	nd	nd	
7	100-120	16.9	2.4	10	40	1.0	24	5.0	99
III 8	0-20	10.0	4.1	58	5	3.2	13	1.7	95
9	40-60	11.3	4.5	60	5	nd	nd	nd	
10	100-120	11.2	4.3	60	5	1.9	9	1.6	93
Red Yellow Latosol									
IV 11	0-20	5.6	2.9	24	39	1.2	29	1.9	104
12	40-60	5.9	2.7	27	40	nd	nd	nd	
13	100-120	5.3	1.9	25	41	1.4	25	2.1	102
V 14	0-20	9.8	4.5	50	5	9.7	13	1.3	93
15	40-60	10.2	5.2	50	5	nd	nd	nd	
16	100-120	10.5	3.6	51	5	7.9	10	1.5	89
VI 17	0-20	8.9	3.4	27	34	4.8	16	1.5	96
18	40-60	8.6	3.3	33	41	nd	nd	nd	
19	100-120	9.4	3.7	33	30	4.2	12	1.6	94

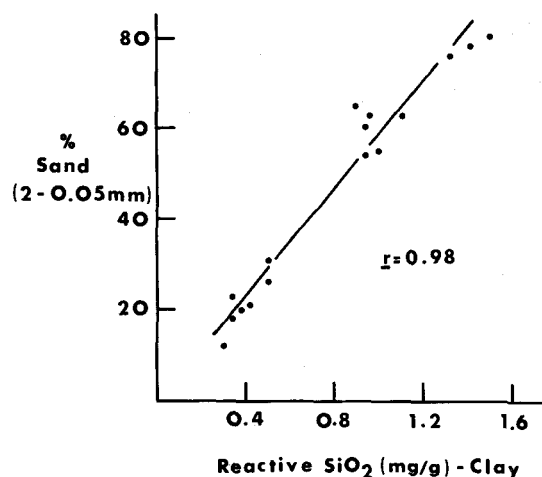
Table 3. Composition of amorphous materials extracted by boiling 0.5 N NaOH and reactive amorphous materials extracted by 0.5 M CaCl<sub>2</sub>, pH 1.5

Profile and sample no.	Depth (cm)	0.5 N NaOH				0.5 M CaCl <sub>2</sub> , pH 1.5			
		SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub> * (Z)	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub> (mg/g)	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>
Dark Red Latosol									
I 2	0-20	8.1	8.6	1.6	1.6	0.42	2.88	0.88	0.25
3	40-60	nd	nd	nd	nd	0.38	3.02	0.48	0.21
4	100-120	11.8	6.0	2.0	3.3	0.51	3.02	0.37	0.28
II 5	0-20	11.9	8.7	0.8	2.3	1.51	3.40	1.54	0.76
6	40-60	nd	nd	nd	nd	1.42	3.32	1.26	0.73
7	100-120	11.6	8.8	0.9	2.2	1.33	3.18	0.92	0.71
III 8	0-20	3.5	5.4	2.9	1.1	0.90	4.76	1.31	0.32
9	40-60	nd	nd	nd	nd	0.96	4.46	0.97	0.37
10	100-120	4.0	1.2	2.6	5.7	1.11	4.70	0.75	0.40
Red Yellow Latosol									
IV 11	0-20	12.9	9.4	3.5	2.3	0.30	3.33	0.80	0.15
12	40-60	nd	nd	nd	nd	0.34	3.33	0.46	0.17
13	100-120	11.3	8.8	2.2	2.2	0.39	3.56	0.34	0.18
V 14	0-20	2.1	4.5	5.1	0.8	0.30	5.15	1.26	0.10
15	40-60	nd	nd	nd	nd	0.34	4.60	0.92	0.12
16	100-120	2.4	2.8	4.0	1.5	0.49	4.60	0.75	0.18
VI 17	0-20	7.3	5.1	1.8	2.5	0.95	4.45	1.20	0.36
18	40-60	nd	nd	nd	nd	0.95	4.24	0.80	0.38
19	100-120	7.0	2.0	2.2	5.9	1.05	4.45	0.57	0.40

\* Corrected for dissolution of gibbsite.

*Relationship of quartz content to clay mineralogy*

The quartz content of the soils was found to have an interesting relationship to the nature of the clay fractions. This was not immediately obvious and it was not necessarily the relationship initially expected. Regression analysis showed that there was little if any relationship ( $r^2 = 0.02$ ) between the sand content (predominantly quartz) and the gibbsite-gibbsite + kaolinite ratios of the clay fractions. Obviously, quartz presence has little influence on gibbsite stability in these soils. However, a high degree of correlation ( $r^2 = 0.96$ ) was found to exist between the sand content and the amount of reactive SiO<sub>2</sub> present in the clay fractions (Fig. 5). This relation is probably a consequence of an extremely slow dissolution of a small amount of quartz over long periods of time. At least a portion of the Si(OH)<sub>4</sub> so produced could have been adsorbed by the aluminous surfaces present

Fig. 5. Relationship of sand (2-0.05 mm) content to reactive SiO<sub>2</sub> content of the clay fractions.

in the clay fractions. It may be more than just coincidence that the reactive SiO<sub>2</sub> content of the clay fractions, 0.30 to 1.51 mg SiO<sub>2</sub>/g (Table 3), is very close to the value of 0.2 to 1.2 mg SiO<sub>2</sub>/g found by Hingston and Raupach (1967) for the adsorption of Si(OH)<sub>4</sub> by gibbsite in the pH range of 4.6 to 6.0.

Because quartz also occurred in the silt fractions and the generally accepted idea of increased solubility with decreasing particle size, it was thought that the silt content might also be related to the reactive SiO<sub>2</sub> content of the clay fraction. The silt fraction, however, seemed to be less related ( $r^2 = 0.59$ ). Apparently, in the present situation, the generally greater mass of quartz in the sand fraction is the determining factor.

Overall, the results tend to confirm the previous suggestions by Kittrick (1969), Brydon and McKeague (1971) and Lodding (1972) that the slow kinetics of dissolution-precipitation prevent quartz from assuming a dominant role in mineral equilibria in soils. On the other hand, the results show that quartz dissolution has been operative in these soils. Even though the dissolution has apparently been of insufficient magnitude to maintain activities of Si(OH)<sub>4</sub> in the soil solution over any extended period of time other than to influence the composition of the reactive surfaces of the clay fractions, the fact that it has occurred, would indicate that quartz is not entirely an inert component in these soils.

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## REFERENCES

- Anderson, J. U. (1963) An improved pretreatment for mineralogical analysis of samples containing organic matter: *Clays and Clay Minerals* **10**, 380-388.

- Brydon, J. E. and McKeague, J. A. (1971) Differences between lateritic and podzolic weathering: a criticism: *Geochim. Cosmochim. Acta* **35**, 1297–1298.
- Cline, M. G. and Buol, S. W. (1973) Soils of the Central Plateau of Brazil and extension of field research conducted near Planaltina, Federal District, to them: *Agronomy Mimeo* pp. 73–17. Cornell University, Ithaca, New York.
- Curtis, C. D. (1970) Differences between lateritic and podzolic weathering: *Geochim. Cosmochim. Acta* **34**, 1353–1356.
- Dolcater, D. L., Syers, J. K., and Jackson, M. L. (1970) Titanium as free oxide and substituted forms in kaolinites and other soil minerals: *Clays and Clay Minerals* **18**, 71–79.
- Dudas, M. J. and Harward, M. E. (1971) Effect of dissolution treatment on standard and soil clays: *Soil Sci. Soc. Am. Proc.* **35**, 134–140.
- FAO–UNESCO (1971) *Soil map of the world—IV: South America*: UNESCO, Paris, France.
- Gardner, L. R. (1970) A chemical model for the origin of gibbsite from kaolinite: *Am. Miner.* **55**, 1380–1389.
- Grewelling, T. and Peech, M. (1965) Chemical soil tests: *Cornell Univ. Agric. Exp. Sta. Bull.* p. 960. N.Y.S. College of Agric. and Life Sci., Ithaca, New York.
- Hashimoto, I. and Jackson, M. L. (1960) Rapid dissolution of allophane and kaolinite–halloysite after dehydration: *Clays and Clay Minerals* **6**, 144–153.
- Hingston, F. J. and Raupach, M. (1967) The reaction between monosilicic acid and aluminum hydroxide—I: Kinetics of adsorption of monosilicic acid by aluminum hydroxide: *Austr. J. Soil Res.* **5**, 295–309.
- Jackson, M. L. (1969) *Soil Chemical Analysis—Advanced Course*, 2nd Edition. Published by the author, Dept. of Soil Science, Univ. of Wisconsin, Madison.
- Kittrick, J. A. (1969) Soil minerals in the  $Al_2O_3$ – $SiO_2$ – $H_2O$  system and a theory of their formation: *Clays and Clay Minerals* **17**, 157–167.
- LeRoux, J. (1973) Quantitative clay mineralogical analysis of Natal Oxisols: *Soil Sci.* **115**, 137–144.
- Lodding, W. (1972) Conditions for direct formation of gibbsite from K–feldspar—discussion: *Am. Miner.* **57**, 292–294.
- McLean, E. O. (1965) Aluminum: In *Methods of Soil Analysis* (Edited by Black C. A. et al.), Part 2, pp. 978–988. Am. Soc. Agron., Madison, WI.
- Siever, R. (1962) Silica solubility, 0–200°C, and the diagenesis of siliceous sediments: *J. Geol.* **70**, 127–150.
- Tweneboah, C. K., Greenland, D. J. and Oades, J. M. (1967) Changes in charge characteristics of soils after treatment with 0.5 M calcium chloride at pH 1.5: *Aust. J. Soil Res.* **5**, 247–261.
- Weaver, R. M. (1973) Mineralogy of highly weathered soils of the humid tropics: In *McGraw-Hill Yearbook of Science and Technology*. p. 379–380. McGraw-Hill, New York.