

EFFECT OF WEATHERING AND PARENT MATERIALS ON CLAY MINERALISATION : RED FERRUGINOUS SOILS OF HUMID TROPICS

by B. DATTA* *College of Agriculture, Calcutta University, Calcutta*
and

M. ADHIKARI, *Department of Applied Chemistry, Calcutta University, Calcutta*

The formation of clay minerals of humid tropical soils of India within the parallels 18°23' and 18°32' latitude and 82°40' and 82°33' longitude, were interpreted in terms of weathering ionic environment. Acid igneous rich in K-feldspars and muscovite is the principal parent material in association with some basic components. Influence of the latter is masked by the drasticity of weathering which introduces H⁺ in large proportion in the exchange complex. The dominance of kaolinite in clays has been associated with the weathering of feldspars present appreciably both in sand and silt separates. Abundance of muscovite in fine sand and appearance of hydro-mica phase in them, indicate mica weathering, another possible mechanism of kaolin formation.

INTRODUCTION

Though the present position regarding the exact reaction-mechanism leading to the formation of clay mineral is still obscure, the role of ionic environment yielded by the weatherable rock-forming minerals in the weathering zone has been unequivocally emphasised and is considered as one of the approaches towards clay mineral genesis. According to Grim (1947), in ionic environment rich in alkaline earth cations set free by the basic igneous rock under insufficient leaching condition, montmorillonite is the product, while in presence of alkali cations, particularly potassium, illite will be formed.

Drastic leaching condition tending to remove these bases away from weathering zone, favours the formation of kaolinite. As is the case of the basic igneous rocks, the same holds equally good for the acid igneous rocks containing alkali and alkaline earth cations under differential weathering conditions.

The purpose of this paper is to relate the mineral species of clays isolated from two Indian red ferruginous soils on different rock types with the mineralogical make-up of their sand and silt separates and to study, in the light of discussion presented above, the nature of ionic environment that led to the formation of secondary mineral in their clays under the prevailing humid tropical weathering condition. To this end, profile samples of soils are analysed for the mineralogical composition of their clays by X-ray, D.T.A, chemical and physico-chemical methods. The mineralogy of coarse silt is studied by X-ray and is supplemented by chemical analysis. The mineral contents of fine sand (50-100 μ), degree of alteration of weatherable minerals in them and a more precise assessment as to the parentage of the soils through provenance study, are worked out (Datta and Adhikari 1968a). A measure

*Present address : Agricultural Engineering Department, Indian Institute of Technology, Kharagpur, West Bengal.

of ionic environment in the soil-forming zone is deduced from soil reaction, and nature and content of exchangeable ion species.

MATERIALS AND METHODS

The soils included in this study were the red ferruginous soils from Manchkund and Padwa (Koraput, Orissa) belonging to humid regions. Characteristic physical and chemical data of the profiles and other details about the climate have been described earlier (Datta and Adhikari 1968 *b*).

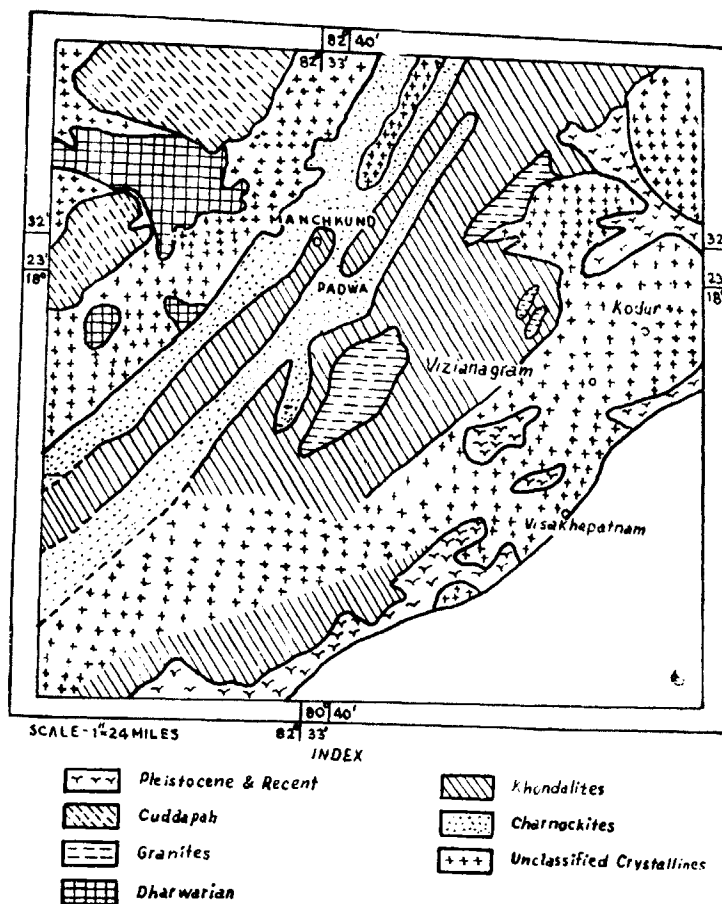


FIG. 1. Geological sketch map around Manchkund and Padwa Dist., Koraput, Orissa (After Map G.S.I. 1961)

Geology

The ancient country rock is mainly ferruginous-schists (Krishnan 1960) containing much haematite and limonite and bands of garnet-magnetite rocks. The country rocks are intervened in monotonous repetition by alternating bands of a host of well-developed Archaean rocks of Eastern Ghats.

The principal groups are garnet sillimanite-schists and gneisses (khondalite series), charnockites series, calc-gneisses and gneissosegranites (Fig. 1).

Sample preparation for X-ray and D.T.A. = clay fractions ($< 2 \mu$) obtained by the international method were converted into H-clay by treatment with 0.05 N HCl and subsequent washing and centrifuging.

Coarse silt (20 – 50 μ) separated from sand by wet-sieving through 300 mesh sieve and repeated decantation (Jackson 1956) was cleansed of free oxides by the method of Aguilera and Jackson (1953).

The entire clay ($< 2 \mu$ size) and coarse silt were subjected to X-ray using nickel-filtered Cu K α radiation and Philip's large Debye-scherrer powder camera (dia. 114.83 mm).

Differential thermal diagrams of organic matter free clay in the H-form were obtained with the help of a manually operated D.T.A. apparatus.

Surface area

Total and external surfaces of oxides-free clays were determined following the procedure of Dyal and Hendricks (1950). Y-value of soil clays was calculated according to the formula given by Martin and Russel (1952).

Chemical analysis

A complete chemical analysis of the entire clay fraction was carried out by Na₂CO₃ fusion method (Robinson 1939).

Free oxides were extracted by the reduction-chelation method (Aguilera and Jackson 1953) and free iron from it determined volumetrically.

Coarse silt was fused with Na₂CO₃. K was determined by flame photometer. Ca and Mg were estimated by versenate titration.

Cation exchange capacity was determined by Ammonium acetate method as given by Peech *et al.* (1947). Exchangeable Ca and Mg were determined by versenate, Na flame photometrically and K by cobaltinitrite method (Jackson 1958).

RESULTS

Base-exchange behaviour of whole soil (Table I)—In Manchkund and Padwa soils, belonging to the humid zone, favourable leaching condition prevails so that H⁺ constitutes a major fraction of the total exchangeable cations. Percentage adsorption of exchangeable calcium and magnesium is fairly low in comparison to that in arid tropical soils (Datta and Adhikari 1968 *a, b*). Potassium saturation is also low. The distribution of exchangeable Ca, Mg and K along the profile is essentially the same in both the soils.

C. E. C., internal surface and Y-value—The results are given in Table II. The values of C. E. C. of Manchkund soil clays compare closely with those of illite (Grim 1953). These values in conjunction with internal surface areas further point to the same. Padwa soil clay as judged from its characteristic exchange capacity and internal surface is most likely to contain illitic clay mineral. The low Y-values of 9 (Manchkund) and 5.8 (Padwa) are, however, indicative of kaolinite occurring also as an important component together with illite.

TABLE I
Base exchange properties of whole soils (oven-dry basis)

Sample	Depth (cm)	Percent absorbed cations					Base saturation at pH 7.0 (per cent)	*C.E.C. at pH 7.0	pH
		Ca	Mg	K	Na	H			
Manchkund	0-15	14.57	11.22	3.19	5.48	65.50	34.46	20.2	6.42
	15-60	16.56	12.78	3.28	6.08	61.30	38.70	14.8	5.96
	60-120	32.99	21.20	6.02	5.46	34.22	65.68	14.5	5.57
Padwa	0-15	16.62	20.19	2.07	7.75	53.37	46.63	11.7	5.99
	30-120	38.98	23.32	3.98	4.78	28.94	71.06	13.4	5.20

*NH₄-exchange capacity

TABLE II
Ethylene glycol retention, C.E.C. and Y-value of soil clay

Sample	Depth (cm)	Total surface		External surface		Internal surface		C.E.C (meq per cent)	Y-value (surface layer)
		(g/g)	(sq.m/g)	(g/g)	(sq.m/g)	(g/g)	(sq.m/g)		
Manchkund	0-15	0.0423	136.6	0.0163	52.6	0.0260	84.0	20.5	
	15-60	0.0451	145.7	0.0266	86.0	0.0185	59.7	18.2	9.0
	60-120	0.0478	154.2	0.0321	103.5	0.0157	50.7	21.7	
Padwa	0-15	0.0322	103.7	0.0273	88.1	0.0048	15.6	29.3	
	30-120	0.0392	126.4	0.0173	55.9	0.0219	70.5	26.3	5.8

TABLE III
Elemental analysis of soil clay (oven-dry basis)

Sample	Depth (cm)	Percentage of							Ignition loss	SiO ₂ /Al ₂ O ₃ molar ratio	Free oxides of iron as Fe ₂ O ₃
		SiO ₂	Al ₂ O ₃	Total	TiO ₂	CaO Fe ₂ O ₃	MgO	K ₂ O			
Manchkund	0-15	38.59	26.82	14.80	3.75	0.54	0.62	3.49	11.19	2.4	2.05
	15-60	36.35	32.15	11.93	0.49	0.23	0.44	4.50	13.00	1.9	6.26
	60-120	40.01	31.36	14.17	0.30	0.26	0.38	2.31	11.97	2.2	1.17
Padwa	0-15	36.66	32.72	13.74	0.54	0.37	0.71	2.11	12.35	1.9	3.97
	30-120	39.60	33.46	12.49	0.50	0.40	0.79	1.54	12.47	2.0	4.66

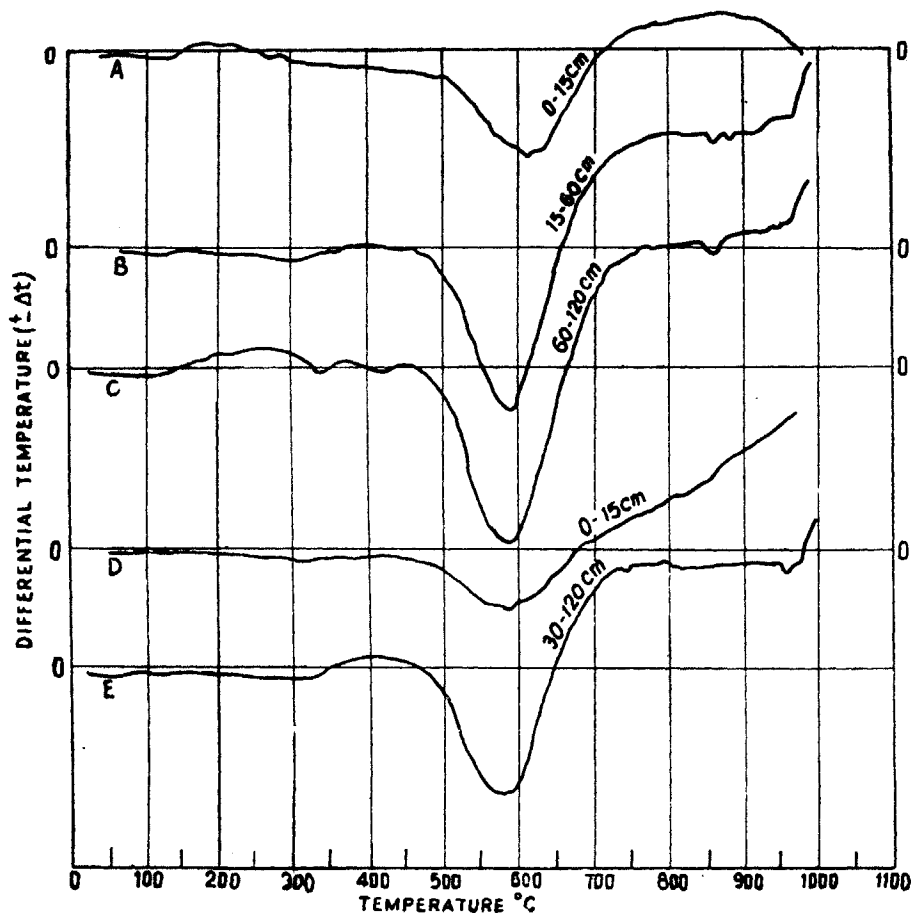


FIG. 2. Differential thermographs of H-clays A, B, C : Manchkund ; D, E : Padwa

Chemical analysis of soil clays—Silica and silica alumina ratio (Table III) clearly indicates the presence of 1 : 1 type clay mineral in both the soils. A good amount of K_2O in Manchkund clay points to the presence of illite as well.

Mineral in soil clays: X-ray—Lattice spacings and their relative intensities are given in Table V. The diffraction pattern for Manchkund clay shows strong reflection at 7.11Å (001), 3.55Å (002) and 2.57Å and (060) reflection at 1.49Å . All these indicate presence of Kaolinite. The fine intensity and sharpness further disclose that Kaolinite present is of well crystallised form. Kaolinite is confirmed on heating to 600°C which marked the elimination of the pattern. A diffuse spacing at 10Å with other reflections at 4.38 , 3.55 (003) and 2.67Å (004) indicates illite. In view of the diffuse nature of (001) reflection and its intensity, it may be inferred that the illite is degraded.

In Padwa clay, the mineral appears to be essentially kaolinitic which is inferred from the strong intensity first order basal reflection at 7.12Å and 002 and 003 spacings at 3.57 and 2.40Å , respectively. Besides kaolinite, there is a trace amount of illite, the existence and quantity of which is detected from its very weak (001) reflection.

TABLE IV
Partial chemical analysis of coarse silt (oven-dry basis)

Sample	Depth (cm)	C.E.C. (meq/100 g)	Percentage of		
			Potassium	Magnesium	Calcium
Manchkund	0-15	2.2	1.6	0.56	-
	15-60	2.4	1.8	0.39	-
	60-120	2.2	2.5	0.33	-
Padwa	0-15	3.9	2.4	-	-
	30-120	3.5	2.2	-	-

D. T. A. study—The D. T. A. curves (Fig. 2) of Manchkund (15-60 cm and 60-120 cm) and Padwa (30-120 cm) are almost flat upto about 500°C, showing little loss of water at low temperature but give sharp endothermic peak between 567 and 602°C corresponding to dehydroxylation reaction. The latter endothermic feature followed by an exothermic reaction at 980°C indicates that the major mineral is well crystallised kaolinite in these clays.

The 0-15 cm samples from both the soils show, unlike the other layers, a very weak low temperature endotherm. This character together with the broad and hump-like dehydroxylation endotherm not typically sharp and intense like that usually encountered with kaolinite, and absence of exothermic reaction may indicate the presence of illite as impurity in a predominantly kaolinitic clay. A similar type of curve behaviour with the D.T.A. curves of mixtures of illite and kaolinite was also noted by Grim (1947).

Minerals in coarse silt—X-ray data are given in Table V. The study shows that quartz is the predominant mineral in 20-50 μ fractions of both the soils. Accompanying minerals are feldspars (Brown 1961) and mica, with a greater abundance of the former in Manchkund silt. Potash content (cf Table IV) of this size fraction in different layers also substantiates that a fair amount of K-bearing minerals is present. Potash content and simultaneous absence of Ca indicate that feldspars present are only of K-bearing types and no Ca-plagioclase is present. Mica in these samples does not appear to be one of typical primary micas which normally give well defined basal reflections. Presence of mica here, is detected from a reflection at 10.987 Å and 11.354 Å in Manchkund and Padwa, respectively. No subsequent lower order basal spacings could be obtained. The (001) spacings as obtained, being larger than the usual values (9.9 Å, 10 Å) for mica, indicate that mica present is possibly hydrated or interstratified. Exchange capacity (cf Table IV) also accounts for the presence of a small amount of such secondary mineral in silt.

DISCUSSIONS

These soils are developed *in situ* from the Archaean rocks of the Eastern Ghat (Krishnan 1960) under humid climatic condition. The underlying parent material

TABLE V

Lattice spacing in \AA and their relative intensities in powder diagrams

Soil	H-clay				Coarse silt			
	Lattice spacing comparable with kaolinite		Lattice spacing comparable with illite		Lattice spacing comparable with felspar group		Lattice spacing comparable with quartz	
	d_{hkl}	I	d_{hkl}	I	d_{hkl}	I	d_{hkl}	I
	7.11	7	10.0	(diffuse)	6.4958	$\frac{1}{2}$	3.3285	10
	3.5503	3	4.3879	5	5.8087	$\frac{1}{2}$	2.7809	1
	2.5743	1	3.5503	4	4.2467	6	2.5916	2
	1.4955	$\frac{1}{2}$	2.6742	$\frac{1}{2}$	3.754	4	2.4609	1
			1.4955	$\frac{1}{2}$	3.474	1	2.2939	1
					3.2268	3	2.251	$\frac{1}{2}$
					2.9975	$1\frac{1}{2}$	2.1281	2
					2.9042	$1\frac{1}{2}$	1.9910	1
							1.9363	$\frac{1}{2}$
							1.8253	$4\frac{1}{2}$
							1.8064	4
							1.6822	3
							1.5480	5
							1.5025	$\frac{1}{2}$
							1.4588	1
							1.3789	7
							1.2901	$1\frac{1}{2}$
							3.3285	10
	7.1204	10					2.4518	5
	4.48	5	10.0 (very diffuse)		4.2029	7	2.2805	5
	4.1295	3	4.5997	3			2.2317	3
	3.5785	3	3.3507	1			2.1252	5
	2.40	5	1.4955	6			1.9811	5
	2.4926	4					1.8151	6
	2.2939	2					1.6749	5
Padwa (0-15 cm)	2.0112	2					1.5438	6
	1.4955	6					1.4572	$2\frac{1}{2}$
							1.3774	$6\frac{1}{2}$
							1.2925	3
							1.259	4
							1.2325	3
							1.2031	5
							1.185	$5\frac{1}{2}$
							1.157	$3\frac{1}{2}$

I - Intensity of lines

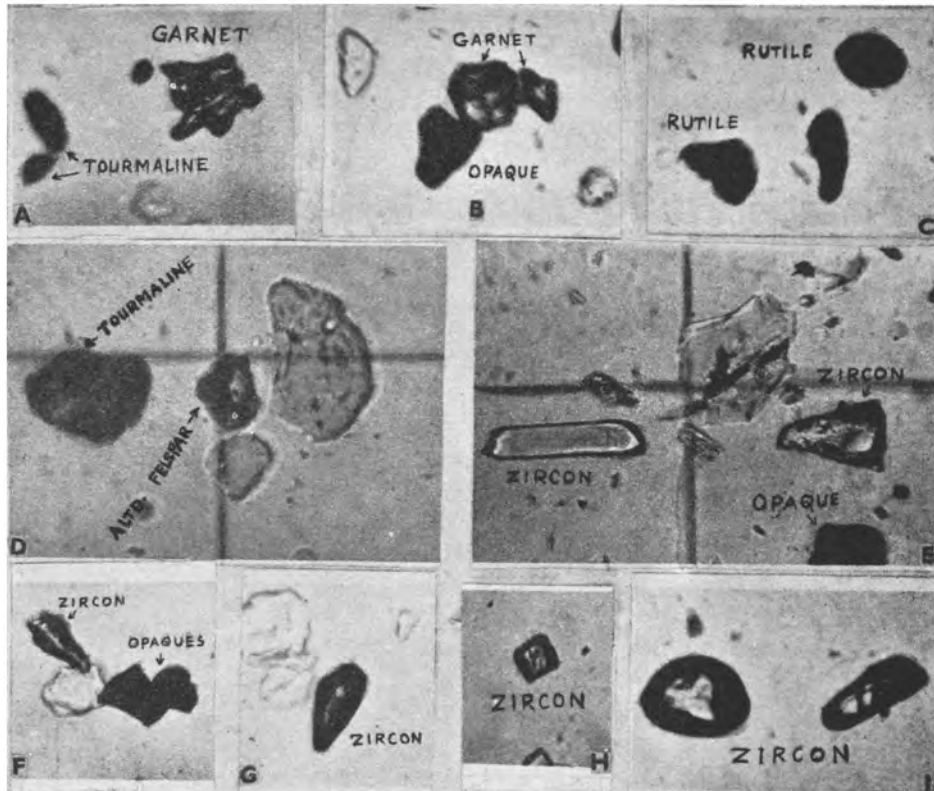


FIG. 3. Photomicrograph of heavy minerals in fine sand (plane polarised light). A-E. Padwa : A, Garnet and tourmaline. $\times 140$; B, Garnet and opaque. $\times 154$; C, Rutiles $\times 78$; D, Tourmaline and altered felspar. $\times 186$; E, Zircons and opaques. $\times 74$; F-I. Manchkund : F, Zircons and opaques. $\times 218$; G, Zircon. $\times 125$; H, Zircon. $\times 114$; I, Zircons. $\times 138$.

is composed mainly of acid igneous and some mixed metamorphic rocks (Datta and Adhikari 1968a). The latter are mainly mica-schist with a minor amount of tremolite-schist in Manchkund and calc-gneiss in case of Padwa. The dominating influence of the parent rocks is reflected in the accessory mineral suite of the fine sands where a conspicuous abundance of zircon (Fig. 3), in particular, points to the presence of acidic parent material. The latter are also highly rich in K-feldspars and muscovite, K-feldspars being in states of alteration. Compared to K-feldspars plagioclase occurs in very small amount. It is chiefly basic (towards anorthite in Padwa) and fairly altered.

Adherence of a fair amount of K-feldspars and total extinction of plagioclase in silt size fraction indicates more weatherability of soda-lime feldspars compared to their potassium analogues. This may also suggest that silt fractions of these soils are chemically more reactive than their sand fractions.

Distinctly acid reaction and good content of free oxides of iron (Table III) in association with clay particles indicate an intense weathering condition of leaching. Whatever Ca^{++} , Mg^{++} and K^+ are set free by the basic and K-bearing components of the parent rock, might have been, under this circumstances, removed away from the weathering zone of the soils. As a result, influence of parent material containing basic component (of calc schist) whatever little is there is masked and H-ions constitute a large proportion of the exchangeable bases.

The dominance of kaolinite in these clays appears to be associated with the weathering of feldspars, mainly K-feldspars, present in fair amount in both sand and silt fractions.

Under the prevailing acidic soil environment the hydrolytic decomposition of the feldspars might result in a pronounced leaching of bases, particularly K and Ca, leading finally to the production of kaolinite (Keller 1964). Similar conclusion was arrived at by De Kimpe *et al.* (1961) Keller *et al.* (1963), and Correns (1963).

When mica weathers, H^+ gradually replaces K^+ and the mineral is hydrated forming hydro-mica (Bates 1960) ultimately passing on to kaolin. Large abundance of muscovite in fine sands and appearance of hydromica phase (Datta and Adhikari (1968 *a, b*) in them, indicate mica weathering and its possible alteration to kaolin in these soils. This may be another reasonable mechanism of kaolin formation in these soils. It has also been observed by Sand (1956) that micas weather to kaolinite under fairly intensive weathering environment.

Whatever may be the mechanism, it may be inferred that acid granitic parent material and pronounced leaching weathering condition leading to an acid environment, have favoured the formation of kaolin in these soils.

Results go to show that though the mineral composition in both these soils is essentially kaolinitic, the proportion is relatively more in Padwa clay, while in Manchkund it is diluted by a little more illite.

Formed on same nature of parent material and identical climate being within a latitudinal and longitudinal variation range of 9' and 7', respectively (situated at a short distance apart), this minor but tangible variation is interesting to note. This anomaly can be explained if we take into account the greater intensity of leaching weathering condition in Padwa soil as evidenced from comparatively lower pH, and higher clay content and free oxides of iron associated with clay. Variation in these properties under similar set of climatic factors is presumed to have been brought about by some microclimatic influence inside Padwa soil and possibly, the latter bringing forth an enhanced leaching effectiveness that has been responsible for a relatively more content of kaolin as compared to that in Manchkund soil clay.

REFERENCES

- Aguilera, N. H., and Jackson, M. L. (1953). Iron oxide removal from soils and clays. *Proc. Soil Sci. Am.*, **17**, 359-364.
- Bater, T. F. (1960). Rock weathering and clay formation in Hawaii. *In: Mineral Industries*. Pennsylvania State Univ., **29** (8) 1.
- Brown, G. (1961). Other minerals. *In: The X-ray Identification and Crystal structures of Clay Minerals*, Mineralogy, Soc. (Clay Minerals, Group London. pp. 467-488.

- Correns, C. W. (1963). Experiments on the decomposition of silicates and discussion of chemical weathering. *In: Clays and Clay Minerals*(10th Conf.), pp. 443-459. Pergamon New York
- Datta, B., and Adhikari, M. (1968). Relation of parent material and environment to the clay minerals of some Indian soils of arid tropical zone. *Agrokamia Talajian* (supplementum), **17**, 125-141.
- (1968). Effect of weathering and parent materials on clay mineralization : Part I. *Indian J. applied Chemistry.*, **31**, 143-150.
- De Kimpe, C., Gastuche, M. C., and Brindley, S. W. (1961). Ionic coordination in aluminosilicic gels in relation to clay mineral formation. *Am. Min.*, **46**, 1370-1382.
- Dyal, R. S., and Hendricks, S. B. (1950). Total surface of clays in polar liquids as a characteristic index. *Soil Sci.*, **69**, 421-432.
- Grim, R. E. (1947). Differential thermal curves of prepared mixtures of clay minerals. *Am. Min.*, **32**, 493-501.
- (1953). *Clay Mineralogy*. McGraw Hill, New York. pp. 316-347.
- Jackson, M. L. (1956). Mineral fractionation for soils. *In: Soil Chemical Analysis—Advance Course*. Wisconsin Univ., Madison, pp. 101-170.
- (1958). *Soil Chemical Analysis*. Prentice Hall. Englewood Cliffs., New Jersey.
- Keller, W. D. (1964). Processes of origin and alteration of clay minerals. *In: Soil Clay Mineralogy*. (Ed. C. I. Rich and G. W. Kunze). Univ. of North Carolina Press.
- Keller, W. D., Balgord, W. D., and Reesman, A. L. (1963). Dissolved products of artificially pulverised silicate minerals and rocks. Part I. *J. Sed. petro.*, **33**, 191-204.
- Krishnan, M. S. (1960). *Geology of India and Burma*. Higgin Botham, Madras.
- Martin, R. T., and Russel, M. B. (1952). Clay minerals of four Southern New York Soils. *Soil Sci.*, **74**, 267-269.
- Peech, M. *et al.* (1947). *Methods of soil analysis for soil fertility investigation*. USDA Circ. No. 757.
- Robinson, W. O. (1939). *Method and procedure of soil analysis used in the Divn. of soil Chemistry and Physics*. USDA Cire., 139.
- Sand, L. B. (1956). On the genesis of residual kaolin. *Am. Min.*, **41**, 28-40.