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PROFESSOR S.K. MUKHERJEE - Clay Minerals Society of India Foundation Lecture

Clay Mineral Structures : The Beauty of Symmetry and the Enigma of Quasicrystals

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A rare honour is bestowed on a chosen few who are privileged to deliver the Foundation Lecture of any Society. However, getting the opportunity to deliver the first Foundation Lecture is an honour of life time. I am most grateful to you all.

Late Professor S.K. Mukherjee, Founder President of the Clay Minerals Society of India, was my teacher, mentor, doctoral research guide and much more. Several articles have been written on his research contributions and more so, on him as a great human being (Ghosh, 2007a). Being the youngest doctoral student of Professor Mukherjee, I only quote the recorded statement of his first doctoral student, late Dr. A.K. Ganguly, DSc, FNA, *Padmashree*, "I am yet to meet as perfect a gentleman as my teacher and friend, Sushil Mukherjee".

Systematic research on clay mineralogy in India was initiated by late Professor J.N. Mukherjee, teacher and doctoral research guide of Professor S.K. Mukherjee. The monumental contribution of this internationally acclaimed 'Calcutta School of Colloid Research' has been well documented (Mukherjee, 1983; Ghosh, 2007b).

In the early eighties, a few dedicated persons with a strong motivation formed the Clay Minerals Society of India in New Delhi with Professor S.K. Mukherjee as the President. In spite of limited number of scientists in this field, the meetings are always informal and satisfying with an air of something new all the time. The main credit, however, should go to the Editors who maintained continuous publication of the journal without compromising the quality. Very recently, the journal *per se* has been assessed by SCOPUS (an unit of Elsevier, Netherlands). The report dated 16 April 2012 states, "the title 'Clay Research' covers a niche area that will be of interest to an international audience." "an admirable journal". This success story of a small Society with a handful of individuals and little resources reaffirm that dedication and class are the key elements.

The Beauty of Symmetry

Symmetry All Around

Human body is beautiful because it is symmetric. Grandeur of *Taj Mahal* roots to its symmetry. Nature is full of symmetry — the wings of the butterfly, flying of the geese or the calling of a cuckoo. In our classical music, when we expand the *raga* by *alaap*, we follow knowingly or unknowingly strictly mathematical symmetric combinations. The cosmic dance is a supreme manifestation of sublime symmetric movements.

Symmetry in Clay Minerals

Clay minerals were considered as amorphous materials even in the first quarter of the last century. With the advancement in x-ray diffraction techniques, they were found to be micro-crystalline. Soon thereafter, their structures were proposed (Pauling, 1930). In the context of the present article, the definition of a crystal that is most apt may be the following. A crystal may be described as a three-dimensional pattern in which a structural motif is repeated in such a way that the environment of every motif is the same throughout the crystal.

Discrete silica tetrahedrons first form a chain and then a sheet, all in symmetric combinations. Similarly, octahedrons of aluminium or iron or magnesium form diotahedral or trioctahedral sheets. Subsequent symmetric combinations of tetrahedral and octahedral sheets result in the formation of unit layers of various clay minerals.

Symmetry in Crystals

A crystal is a substance in which the atoms, molecules or ions are packed in a regularly ordered, repeating three-dimensional pattern. Thus by definition, a crystal is infinite. However, real crystals contain imperfections and are finite.

The aforesaid definition visualizes the formation of crystals by symmetric combination of their smallest building blocks called unit cells. The crystals are, therefore, classified based on the geometry of their unit cells. Initially on the basis of simple 3-D geometry, they are classified into 7 groups called Crystallographic Systems. Further with a little extension of this knowledge, subdivisions are made into 14 Space Lattices. By utilizing the concept of rotation, crystals can be subdivided into 32 Point Groups. Finally by introducing the parameter of translation, classification into 230 Space Groups is possible.

Solid state displays substantial short range and long range symmetry. Long range symmetry, however, is the hallmark of crystallinity. Even purely amorphous materials can have short range orders. Distinction between crystalline and amorphous materials is made by experimental means, usually x-ray diffraction or electron diffraction. Pseudo-crystalline or para-crystalline substances exhibit broad bands or halos in their x-ray diffraction patterns instead of sharp bands.

Briefly, most essential characteristic of a crystal is their space group symmetry, 230 Space Groups. Among the rotational symmetries, 2-, 3-, 4- and 6-fold axes are allowed while 5-, 7- and all higher rotational axes are not allowed; 5-fold symmetry is incompatible with translational symmetry. Icosahedral symmetry is the most forbidden crystal symmetry because it incorporates the largest possible number (6) of the independent axes of 5-fold symmetry.

The Enigma of Quasicrystals

The Great Puzzle

Dan Shechtman, an Israeli Chemist, and his coworkers noted with great surprise that an alloy of aluminium and manganese, Al_6Mn, produced a diffraction pattern of sharp spots like a crystal but with the symmetry of an icosahedron (Shechtman *et al.,* 1984). The finding contradicts the well-established theorems of crystallography which are hundred years old and their mathematical basis dates back to over two hundred years. Shechtman had all the trouble in publishing the observations (Shechtman *et al.*, 1984) and even thereafter it took quite a while to publish the details and justification (Shechtman and Blech, 1985). Levine and Steinhardt (1984) coined the term 'quasicrystals' and called them a new class of ordered structures.

The War

The hell, as expected, broke loose. Linus Pauling was one of the first to challenge the existence of quasicrystals. According to him, directed multiple twinning of cubic crystals resulted in apparent icosahedral symmetry (Pauling, 1985). Even Shechtman and Blech (1985) opted for a relatively non-controversial route by proposing glassy arrangement of icosahedral clusters. Although others reported synthesis of quasicrystals, general skepticism remained. The primary objection was that these quasicrystals are prepared under sophisticated highly controlled chemical environment and they are delicate metastable compounds; they cannot be classified as stable robust crystals.

The Armistice

Incidentally, there was a clue. In the early seventies, famous philosopher and mathematician, Roger Penrose, proposed quasiperiodic patterns which are free to violate the theorems that govern crystal symmetry (Penrose, 1974). This currently famous 'Penrose tiling' comprises two tiles arranged quasiperiodically in a five-fold symmetric pattern.

Tsai *et al.* (1987) first reported a stable quasicrystal in an aluminium-copper-iron alloy system and this stability characteristic resolved the cynicism cited above. Quasicrystals are nowadays generally accepted as ordered but not periodic structures which allow all kinds of forbidden crystal symmetries including the icosahedral symmetry.

In appreciation of his discovery of quasicrystals, Dan Shechtman was conferred the Nobel Prize in Chemistry (2011).

Nature the Saviour

In spite of all the battles won or lost, a large number of crytallographers refused to place quasicrystals on the same pedestal with crystals. Nature settled the matter once and for all.

There was a rock sample labelled as 'khatyrkite' in the University of Florence Museum. This was collected from the Khatyrka region of the remote Koryak mountains of the Kamchatka peninsula. The sample contained khatyrkite ($CuAl_2$), cupalite (CuAl), diopside, forsterite, β-AlCuFe and a new phase whose x-ray diffraction did not match with any known mineral. On electron diffraction, however, this unidentified phase exhibited the unmistakable signature of an icosahedral quasicrystal (Bindi *et al.*, 2009). This new mineral is now officially accepted as the first natural quasicrystal and named 'icosahedrite' (Bindi *et al.*, 2011). The compostion, $Al_{63}Cu_{24}Fe_{13}$, matches the first laboratory synthesized quasicrystals but more surprisingly, has the same degree of structural perfection. This is inconceivable in view of highly controlled laboratory conditions under which the quasicrystals are synthesized (Tsai *et al.*, 1987).

The Second War and the Celestial Intervention

The obvious doubt immediately aired by the scientific community was about the genuinity of the source of the rock sample containing icosahedrite. This suspicion was compounded by the presence of metallic aluminium in the sample. As aluminium oxidizes unless placed under artificial reducing conditions, the possibility of a man-made byproduct particularly a slag cannot be ruled out.

In 2011, a team of geologists from USA, Russia and Italy visited the exact reported source in that remote region of Koryak mountains, far from industrial or any other anthropogenic activity. They collected huge quantity of samples and found icosahedrite (Bindi and Steinhardt, 2012). This along with exhaustive investigation of the original rock sample settled the slag hypothesis.

The most exciting observation is the inclusion of quasicrystal grains within stishovite, a polymorph of SiO_2 which forms only under ultra-high pressures (> 10 Gpa). Subsequent age determination concluded that they were formed > 4.5 billion years ago, coincident with the creation of Planetary System (Bindi *et al.*, 2012). This is a clear evidence that the quasicrystals intergrown with silicates and oxides are extra-terrestrial. This remarkable discovery of spontaneous formation of quasicrystals under natural conditions and survival over geologic timescale is simply baffling.

The Hunch in Clay Mineralogy

Can we expect quasicrystal features in clay minerals? The chances are remote but the dreams are always wild. Intuitively, two areas are to be kept under surveillance. The remarkable proposition of Varadachari (2006) that for non-stoichiometric variable composition materials like clay minerals, the two phases in a phase diagram cannot be separated by a line but by a zone. This strikingly novel idea is not an addition of knowledge only to clay mineralogy but to the physical chemistry itself. The fuzzy zones wherein the gradual transformation from one clay mineral to another occurs, may be probed.

The amorphous clay minerals are divided into two classes, purely amorphous like allophanes and pseudo-crystalline like imogolite. Silicon here is invariably in tetra-coordination while aluminium can be either in hexa- or tetra-coordination. The increased degree of tetra-coordinated aluminium increases the amorphous character. Here also, instinct suggests that controlled chemistry of tetra-coordinated aluminium is worth exploring.

The Revelation

Research at the ultimate superlative level like developing a drug for an incurable disease or designing a system to produce hitherto unknown critical information is unequivocally exceptional. But these quasicrystals have brought us to the precipice. Hundred years of class room teaching in physics, chemistry, geology or engineering on a subject thought to be of solid foundation coupled with another hundred years of rigorous mathematical back up have been countered head on. Rarely we are dumbfounded to note that one of our greatest recent achievements of synthesizing something, stunningly new but often unstable, under strictly controlled artificial conditions has long been produced and protected by Mother Nature over a few billions of years. Even more rarely we converge at the crossroad of science and philosophy. The quasicrystals have revolutionized our outlook about possible forms of matter. Also, this may only be the tip of the iceberg. Who knows what is in the store? To conclude, I quote "The objects which we see and touch in everyday life are only shadows" (*Upanishad*).

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An *ab initio* Approach to Construct Clay Mineral Structures : II. Pyrophyllite

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Abstract : *A theoretical approach, which does not require any experimental data, can be an ideal tool for supplementing experimentally derived information on crystal structures of clay minerals and provide fine details of crystal structures which often cannot be obtained by experimentation . Earlier, an ab initio quantum mechanical technique based on density functional theory (DFT) was utilized to develop the crystal structure of a 1:1 type clay mineral, kaolinite, followed by the evaluation of its crystal properties. The outcome and validation, were encouraging. Here, the same concept has been adapted to a 2:1 type clay mineral, pyrophyllite.*

In an earlier paper (Varadachari *et al.*, 2011), we attempted to introduce a new approach to the study of clay minerals, involving *ab initio* derivation of the detailed crystal structure and ground state properties of layer lattice silicates, based on full-potential linearized augmented plane-wave method . Essentially, (i) a method was developed for deriving the crystal structure of clay minerals based initially on a 1:1 type mineral, viz., kaolinite. An optimized crystal structure was built up theoretically and crystal properties were derived by subsequent theoretical methods, (ii) the derived crystal properties were validated with available literature, (iii) some crystal parameters, not yet determined by any experimental method, were evaluated. In order to fulfill the final objective of the earlier work (Varadachari *et al.*, 2011), an attempt has been made here to extend the developed concept to a 2 :1 type clay mineral, viz, pyrophyllite, an end-member.

Methodology

The theoretical basis of the method employed has earlier been discussed in detail (Varadachari *et al.*, 2011). In brief, local spin density approximation (LSDA) within density functional theory or DFT (Hohenberg and Kohn, 1964; Kohn and Sham, 1965) has been employed for solving the many-electron problem of a crystal (with nuclei at fixed positions).

A parallel computing system with 8-node cluster (Pentium IV of 3 GHz with 2GB RAM) was installed with Red Hat 9 and Beowulf architecture for clustering. The clustering software used was Oscar 4.1. Supporting software needed for running the *ab initio* program include, Fortran compilers and Intel Cluster MKL for parallel data processing. *Ab initio* derivations were done using *Wien 2k* (Version 09) and structure visualization with *Xcrysden* (Varadachari and Bhowmick, 2009).

Electronic structure calculations of solids were based on DFT. The program *Wien2k* which is based on the full-potential linearized augmented plane-wave (FP-LAPW) method (Blaha *et al.*, 2001) was used. The FP-LAPW method solves the Kohn-Sham equations for ground state density, total energy and eigenvalues (energy bands) of many-electron systems by introducing a basis set which is especially adapted to the problem (Martin, 2004). Solutions to the Kohn-Sham equations are obtained self-consistently by an iterative process under the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof functional for the exchange-correlation energy and subject to periodic lattice boundary condition.

Pyrophyllite has the chemical formula [Si_8 Al_4 O_{20} $(OH)_4$] and a tetrahedral-octahedral-tetrahedral (t-o-t) structure. Derivations considered a unit cell of pyrophyllite with 40 atoms and no symmetry operators. Thus, the structure of pyrophyllite was adjusted to reflect P1 symmetry.

Basic inputs for derivations

Prior to deriving the crystal properties, input parameters were optimized followed by optimization of unit cell dimensions . The required input parameters were :

(i) Rmt (muffin-tin radius) : This can be estimated after running NN (nearest neighbour program). The spheres were chosen as large as possible to save computer time. The Rmt values taken in this study were Rmt (Al) = 1.82 Å, Rmt (O) = 1.08 Å, Rmt (Si) = 1.51 Å, Rmt (H) =0.58Å.

(ii) RKmax (Rmt *kmax) : determines the number of basis functions (size of the matrices), where kmax is the plane wave cut-off, Rmt is the smallest of all atomic sphere radii. The derived value of optimized RKmax was 2.55.

(iii)KGEN : Program KGEN generated the k-mesh in the irreducible wedge of the Brillouin zone (IBZ). Here the optimized k-points derived was 8; inversion was added.

(iv) Mixing factor = 0.10 (BROYD scheme)

(v) GGA (General Gradient Approximation) =13 [Perdew-Burke-Ernzerhof functional]

(vi) Cut-off energy : The energy cut-off specified between core and semi-core was -9.0 Ry.

(vii) Emin and Emax : The minimum and maximum energies for which the output eigenvectors and eigenenergies would be printed was -9.0 Ry and 2.5 Ry.

Optimization of the cell

For cell optimization, first it was essential to develop a strain free structure of pyrophyllite. The internal atomic coordinates and the cell shape were systematically optimized by the following two consecutive steps, viz., (i) force minimization, and (ii) optimization of lattice constants. The program "mini" (Blaha et al., 2001) was used to determine the equilibrium positions of all individual atoms obeying the symmetry constraints of a certain space group.

Calculations showed that the experimentally derived structure of pyrophyllite (Wardle and Brindley, 1972) had forces of 256.91 mRy/Bohr. Using "mini" program, force minimization was accomplished and we got more relaxed structure with forces 51.50 mRy/Bohr (structure after force minimization). For optimization of lattice constants (a,b,c), the following successive steps were executed using optimized RKmax and k- points (Cottenier 2004) : (a) Optimization of b/a keeping c/a and volume constant, (b) optimization of c/a keeping b/a and volume constant, and (c) optimization of volume.

Theoretical XRD of the minerals were derived using Shape-software ATOMS63 (*version 6.3*) by supplying derived crystallographic inputs like optimized cell parameters, space group and optimized positions of the atoms.

Results and Discussion

Optimized lattice constants were calculated from volume-energy relationship which showed good fitting with Murnaghan's equation of state (Murnaghan, 1944). The computed lattice constants were in good agreement with the experimentally derived values (Wardle and Brindley, 1972) as evident in Table 1. The simulated a axis length and d spacing were nearly equal to those observed experimentally. But the simulated b axis length 9.034 Å was slightly larger than experimental one (Wardle and Brindley, 1972). Experimental density of 2.815 g/cc (Wardle and Brindley, 1972) was quite close to the calculated one, i.e., 2.795 g/cc. The calculated Fermi-energy and binding energy were 0.19473 Ry and -25.34 kJ/mol. The calculated total energy was -55573.73 kJ/mol. After getting optimized crystal structure, several crystallographic properties like bond distance, electron densities and density of unit cell can be designed (Blaha *et al.*, 2001).

In pyrophyllite, calculated lattice parameters reproduced the experimental values reasonably well (Table 1). Theoretical a, b and c parameters match the experimental values. The experimental Al-O and Al-OH bond lengths were also close to the experimental values (Table 2). The theoretical Si-O bond length (T = tetrahedral cation, in this case Si^{+4}) was slightly longer than the experimental values, a problem that had been traced to the perturbative polarization orbitals of tetrahedral cation (Junquera *et al.*, 2001). Calculated tetrahedral sheet thickness was 2.27 Å whereas the experimental value of the same was 2.15 Å (Wardle and Brindley, 1972) .On the other hand, the calculated octahedral sheet thickness was slightly smaller than the experimental value. The different bond lengths of pyrophyllite, i.e., Al-O, Al-OH, Si-O, O-H as calculated were 1.93, 1.88, 1.63 and 0.96 Å respectively and that of kaolinite were 1.96, 1.86, 1.64 and 0.96 Å respectively (Varadachari *et al.*, 2011). The theoretically derived data are, by and large, in good agreement with the experimental values (Tables 1 and 2) and point to the accuracy of the derivations. Small deviations from experimental values are expected – these reflect the effect of temperature on structural perturbations since calculations done here are for a ground state structure (at 0K).

Table 1 : Unit cell parameters of pyrophyllite

Mineral Parameters	Calculated (ground state 0K)	Experimental (298K)
a axis length(Å)	5.168	5.160
b axis length(Å)	9.034	8.966
layer d spacing (Å)	9.268	9.347
density(g cc^{-1})	2.795	2.815
Fermi Energy (Ry)	0.19473	NA
Binding Energy (kJ/mol)	-25.34	NA
Total Energy (kJ/mol)	-55573.73	NA
Interstitial Charge (eV/atom)	5.42	NA
Charge of Al (eV)	2.37	NA
Charge of Si (eV)	3.29	NA
Charge of O (eV)	2.89	NA
Charge of H (eV)	0.84	NA

NA=Not Available

Table 2. Bond distances (Å) of pyrophyllite

Bonds	Calculated (ground state 0K)	Experimental (298K)
Si-O	1.63	1.62
Al-O	1.93	1.94
O-H	0.96	0.97
Al-OH	1.88	1.89
Interlayer thickness	2.93	2.75
Tetrahedral sheet thickness	2.27	2.15
Octahedral sheet thickness	1.88	2.08

Table 3. XRD analysis of pyrophyllite

Plane (h k l)	*d (theoretical) [Å]*	*d (experimental) [Å]*
001	9.19	9.33
002	4.59	4.67
022	3.17	3.12
-221	2.22	2.23
201	2.34	2.33
-1-3 3	2.09	2.10

The XRD bands as calculated solely on the basis of theoretically derived structure are in excellent agreement with the experimental data (Table 3).

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Elemental Composition and Mineralogy of Silt and Clay Fractions of Cracking Clay Soils of Semi Arid and Arid Parts of Gujarat, India

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Abstract: *Elemental composition and mineralogy of silt and clay fractions in two basaltic Vertisols viz Semla series: Aridic Haplusterts and Sokhda series: Calcic Haplusterts from semi-arid and arid tracts respectively of Gujarat were studied to characterize the nature and composition of clay minerals in relation to elemental composition and to derive geochemical climofunctions. The most reactive fine clay had smectite with traces of quartz and mica whereas concentrations of CaO and Na_2O contents in silt fractions indicating intensive weathering of calcium and sodium minerals. The chemical data further supported the formation of montmorillonite-beidellite group(molar ratio of Al/Al+Fe >0.5 in fine clay fracion). The high degree of salinisation (CaO/K_2O) in Sokhda series indicated the prevalence of high evapotranspiration and prolonged dry seasons in the region. The CALMAG index supported the formation smecite under past humid climate but preserved even in existing alternate wet and dry seasons.*

Key words : *Geochemistry, vertisols, mineralogy, weathering indices*

The geochemistry and mineralogy of Vertisols is of considerable interest because of their wide distribution (72 million hectares) and agricultural use in India. The Deccan basaltic clay soils have dominant smectite clay mineral (Pal and Desphande, 1987; Satyavathi *et al.*, 2010) but later found that the clays contained predominant amounts of the intermediate montmorillonite-beidellite group (Bhattacharyya *et al.*, 1993). These soils under alkaline conditions have high iron in their crystal lattice (Krishnamurthi and Satyanarayana, 1969) where as under anoxic conditions, iron is replaced by magnesium(Van Breemen, 1980). Pedogenic smectite forms in poorly drained soils characterized by high pH with high chemical activity of silica and basic cations (Borchardt, 1989). Minerals of intermediate weathering may be used as indicators of climate change in Southern and Central peninsular India (Pal *et al.*, 1989 and Srivastava *et al.*, 1998). The slow dissolution of Ca zeolites (<1me Ca L^{-1} in distilled water, Pal *et al.*, 2006) provide sufficient bases to prevent compete transformation of smectite in vertisols of humid tropics of western India (Bhattacharyya *et al.*, 2005). The soils in arid climates shows a progressive formation of pedogenic carbonates with concomitant increase in Na ions in soil solution (Pal *et al.*, 2009). Larger differences in octahedral cation composition and in the proportion of aluminum in tetrahedral position of smectites have attributed to weathering environments under which they occur(Mermut *et al.*, 1984). It was further reported that the octahedral cation occupancy together with the number of Mg and Fe atoms per cell decreases with decrease in particle size of soil fractions (Curtin and Smillie, 1981). Therefore, an attempt is made to explore major elemental distribution in silt and clay fractions of smectite dominated basaltic vertisols to discuss changes in chemical composition during pedogenesis and to infer geochemical climofunctions.

Materials and Methods

The two dominant soil series *viz.*, Semla (P1) from semi-arid dry (MAR ≥635mm, mean air temperature (MAT) of 26.7°C, Aridic Haplusterts) and Sokhda (P2) from arid (MARe≥533mm and MAT 26.7°C, Calcic Haplusterts) regions of Gujarat were selected for elemental composition and mineralogical investigations in relation to particle size. These soils were developed over basalt with dark greyish brown to brown, clay textured, moderate, medium, subangular blocky structures in Ap horizons and very dark brown (P1) to dark reddish brown (P2) strong medium angular blocky structures in slickensided Bss horizons enriched with fine common lime nodules (Table 1). The morphological, physical and chemical properties of these soils were described earlier (Satyavathi *et al.*, 2005).

The particle size distribution was determined as per International Pipette method after removal of organic matter, calcium carbonate and iron oxides. Sand (2000-50µm), coarse silt (50-20µm), medium silt (20-6µm), fine silt (6-2µm), coarse plus medium clay (2 to 0.2 µm) and fine clay (<0.2µm) fractions were separated according to size segregation procedure (Jackson, 1979). The elemental composition in different silt and clay fractions was determined using HF and aqua regia acid digestion (Page *et al.,* 1982). Mineralogy of silt and clay fractions was carried out by X-ray diffraction analyses of oriented aggregates saturated with either Ca or K using Philips diffractometer with Ni filtered CuKá at a scanning speed of 2^{0}2è/min. The minerals were identified using the diagnostic methods of Jackson (1979) and Brown (1984). Semi-quantitative estimates of minerals in the clay and silt size fractions were carried out as per the method of Gjems (1967).

Table 1. *Morphology of soils*

Depth (cm)	Horizon	Colour(moist)	Texture	Structure	consistence	Lime nodules	Other features
P1.Semla –Aridic Haplusterts(22^{0}01'59" N -70^{0}48'22"E, mean annual rain fall-635mm, mean annual temperature-26.7^{0}C							
0-17	Ap	10YR2/2	Clay loam	2msbk	sh, fr, s,p	Few, medium	
17-42	Bw1	10YR2/2	Silty clay	2msbk	fr, s,p	Fine-many, few-medium	Shiny pressure faces on ped surfaces
42-57	Bw2	10YR2/2	clay	2mabk	fr, s,p	Fine, very fine-many, few-medium	Shiny pressure faces on ped surfaces
57-86	Bss1	10YR2/2	Silty clay	3cabk	fr, s, p	Very fine –many, few-medium	Wedge shaped aggregates, presence of slickensides
86-115	Bss2	10YR2/2	Silty clay	3cabk	fr, s, p	Very fine-many, few-fine/medium	Wedge shaped aggregates, presence of slickensides
115-144	Bss3	10YR2/2	Silty clay	3cabk	fr, vs,vp	Very fine-many, few-medium	Wedge shaped aggregates, presence of slickensides
144-155	BC	10YR4/2	Clay loam	1msbk	fr, s,p	Very fine-many, few-medium	Powdery lime present in patches
P2.Sokhda- Calcic Haplusterts (23^{o}02'19" N – 70^{04}7'30"E, , mean annual rain fall-533mm, mean annual temperature, 26.7^{0}C							
0-11	Ap	10YR4/2	Clay loam	1msbk	sh, fr, s,p	Few, medium	
11-37	Bw1	10YR3/2	clay loam	2msbk	fr, s,p	Fine-common, few-medium	Shiny pressure faces on ped surfaces
37-63	Bw2	10YR3/3	clay	3msbk	fr, s,p	Fine, very fine-common, few-medium	Shiny pressure faces on ped surfaces, wedge shaped, slickensides
63-98	Bss1	10YR3/3	clay	3mabk	fr, s, p	Very fine –common, few-medium	Wedge shaped aggregates, presence of slickensides
98-145	Bss2	10YR3/3	clay	3mabk	fr, s, p	Very fine-common, few-fine/medium	Wedge shaped aggregates, presence of slickensides
145-160	BC	5YR3/4	clay	2msbk	fr, s, p	Very fine, fine -common, few-medium	

Results and Discussion

Particle size distribution

The sand content is 7.3 to 23.7% in Semla series (P1) and 8.5 to 37.3% in Sokhda series (P2) with depthwise decreasing trends (Table 2). The sand content in cambic and slickensided zones of Semla series (P1, 7.3 to 9.5%) is three times less than in Sokhda aeries (P2). Semla soil (P1) has 26 to 33% silt and 37 to 67% clay with irregular depth trends whereas Sokhda series (P2) has 20 to 43% silt and 41 to 55 % clay. Among silt fractions, medium silt is 9.2 to 15.8 % in P1 and 9.6 to 16.7% in P2 with erratic distribution. The clay content in control section (25 to 100 cm) has more than 60 per cent in Semla (P1) but 45 to 55 per cent in Sokhdal (P2). The fine clay is 70 to 80 per cent of total clay with irregular distribution in P1 and increasing trends in P2. Both soils have 2 to 9 per cent of coarse clay (2 to 0.6μm) and 4.3 to 14.6 per cent of medium clay (0.6 to 0.2μm). These soils are interpreted as vertic palesols based on high clay content (>40% to 60%), most of which is smectite accompanied by intersecting slickensides and mukkara structure(Soil Survey Staff 1999). These basaltic clay soils have coefficient of linear extensibility (COLE) values >0.10, supporting the presence of slickensides(designated as Bss), pedogenic carbonates (k) and seasonal wetness(g). The low matrix chroma(<2) is commonly linked with seasonal saturation and represent the environmentally controlled differences in iron bearing minerals. The estimated hydraulic conductivity is 2.3 cm/h in Ap horizons but reduced to 0.9cm/h in slickensided B horizons at 115 to 144 cm in P1 but decreased from 3.2 (Ap horizons) to 0.2cm/h in P2 at 98 to 145cm (Table 2).

The Semla soil (P1) is mildly alkaline (pH 7.8 to 8.0) with decreasing organic carbon (0.83 to 0.23%), erratic distribution of calcium carbonate (14.5 to 23.3 %), exchangeable Ca/Mg ratio of 1.1 to 2.3, CEC of 37.5 to 53.2 cmol(+)kg^{-1} and exchangeable magnesium per cent of 30 to 45 per cent. On the other hand, Sokhda (P2) is strongly alkaline with exchangeable magnesium per cent of 32 to 51 per cent, CEC of 27 to 32 cmol(+)kg^{-1} and shows slight inflections in organic carbon (0.21 to 0.48%) and calcium carbonate contents (11.6 to 22%). The presence of calcium carbonate nodules are common due to seasonal climates yielding mean annaual precipitation (MAP) between 760mm and 1000mm. The calcitic rhizoliths are common in arid regions where evapotranspiration is greater than effective precipitatio (Srivastava *et al.,* 2002) due to episodic rains that easily solubilise calcium carbonate and micrite precipitates when soil dries (Pal *et al.,* 2009).

Elemental composition and mineralogy

Semla series:

The data shows that Al_2O_3 and Fe_2O_3 are dominant in silt–clay fractions with erratic distribution. The content of Al_2O_3 is

Table 2. *Particle size distribution, available water holding capacity (AWC), hydraulic conductivity (HC) and chemical properties of soils*

Depth (cm)	Particle size distribution (%)							HC (cm/h)	AWC (%)	pH water (1:2)	OC (%)	$CaCO_3$ (%)	EX Ca/Mg	CEC cmol (+)kg^{-1}	EMP
	Sand	Silt			Clay										
	(2000-50μ)	Coarse (50-20μ)	Medium (20-6μ)	Fine (6-2μ)	Coarse (2-0.6μ)	Medium (0.6-0.2μ)	Fine (<0.2μ)								
							P1.Semla								
0-17	23.7	9.3	11.2	12.6	2.6	13.1	27.5	2.3	15.6	7.8	0.83	15.4	2.3	49.5	30
17-42	11.8	5.2	13.8	9.1	5.4	7.2	47.5	4.2	15.5	7.8	0.66	18.2	2.1	50.1	34
42-57	9.5	7.8	9.2	9.8	9.8	2.4	51.5	2.1	13.3	7.9	0.68	18.6	1.4	53.2	41
57-86	7.5	6.4	15.8	9.8	6.2	7.8	46.5	1.7	16.3	7.9	0.48	14.5	2.2	48.3	32
86-115	7.8	2.6	13.2	9.8	5.2	6.7	54.7	3.2	12.5	7.9	0.61	17.2	1.4	52.5	41
115-144	7.3	5.6	14.9	10.4	6.4	6.9	48.5	0.9	14.9	7.9	0.54	17.7	1.7	47.0	35
144-155	21.5	10.9	12.1	18.5	9.2	14.6	13.2	1.2	13.5	8.0	0.23	23.3	1.1	37.5	45
							P2.Sokhda								
0-11	37.3	4.7	10	7.1	5.5	9.4	26	3.2	6.8	8.2	0.48	21.9	2.2	27.6	35.0
11-37	34.6	1.9	11.3	6.8	5.4	5.9	34.1	3.0	12.5	8.4	0.46	21.4	2.3	27.5	32.0
37-63	29.4	3.1	10.5	7.4	4.5	5.4	39.7	1.5	12.7	8.7	0.45	21.5	1.4	28.5	46
63-98	27.3	3.9	9.6	8.5	4.5	6.9	39.3	0.4	14.0	8.8	0.43	22.0	1.0	29.0	47
98-145	23.9	4.2	9.6	7.5	8.0	4.3	42.5	0.2	13.9	8.6	0.25	21.6	0.8	30.3	51
145-160	8.5	9.0	16.7	16.9	7.4	7.1	34.4	2.1	14.0	8.5	0.21	11.6	0.8	32.3	43

10 to 26.4% in coarse silt, 10.6 to 14.9% in medium silt, 13.1 to 16.9 % in fine silt, 15.8 to 20.1 % in coarse plus medium clay and 15.2 to 19.5% in fine clay fractions (Table 3). Similarly, Fe_2O_3 contents vary between 11.4 to 19.8 % in coarse silt and 12.1 to 17.9% in coarse and medium clay fractions showing relatively higher Fe_2O_3 contents in clay fractions. Among bases, CaO is dominant in coarse (4.1 to 16.1%) and medium silt (2.6 to 3.7%) but substantially decreased in coarse plus medium (0.1 to 2.4%) and fine clay fractions (0.1 to 0.7 %). The CaO decreases with particle size due to the less-resistant nature of Ca-rich plagioclase and slow release of Ca from Ca Zeolites that prevents transformation of smectite (Pal *et al.,* 2006). Next to CaO, MgO shows slight variations with depth (2 to 7.7 %) except in coarse silt fractions of Ap horizons (> 10%). The Na_2O contents are relatively high in silt fractions (1.2 to 4.4 %) but decreased to less than 1 per cent in coarse plus medium and fine clay fractions. This leads us to conclude that calcic plagioclases disappear in soil more rapidly than sodic plagioclases, as Ca-rich plagioclase is less resistant to weathering than Na-rich plagioclase. Depletion of CaO and K_2O in clay reflects the greater alteration rate of plagioclase compared to K-feldspar and the formation of illite from plagioclase and micas (Nesbitt *et al.*, 1980). It was reported that silt and clay fractions have close relation with Al_2O_3, Fe_2O_3 and K_2O contents whereas MgO and CaO contents with silt fractions in these basaltic clay soils. Similar kind of relations were reported in basaltic clay soils of Sudan (Blokhuis *et al.,* 1968).

The fine clay contains 99 per cent of smectite with 1 per cent of mica (Table 3) whereas coarse plus medium together contains 58 to 71.5 clay % of smectite whereas coarse silt has 50 to 70% of Na/Ca feldspars, 8 to 16.0 % of K feldspars, 5 to 15% of quartz and 3 to 11% of smectite and fine silt with 28 to 40 % of smectite and 22 to 42 % of Na/Ca feldspars. In general, clay fractions have more smectite whereas silt fractions have high content of feldspars and quartz.

Sokhda series

The Sokhda series shows the dominance of Al_2O_3 in coarse plus medium clay fractions (22.6 % in surface to 28.2 %, Table 4) where as 5.6 to 7.8 % in coarse silt. In coarse plus medium clay fractions, Fe_2O_3 vary from 12.4 to15.8% as against fine silt fraction(8.7 to 13.7%) whereas MgO contents vary 5.3 to 7 % to 4.2 to 4.9%. The CaO in coarse silt contains 0.8 to 2.2 % but decreases with particle size from medium silt (0.5 to 1.3 %) to fine silt (0.2 to 1.1%) and less than 0.1 % in coarse plus medium clay. Na_2O contents in silt fractions is more than 1% but decreased to 0.1 % in fine clay. The K_2O contents are more than 2% in coarse plus medium clay, >1.5 % in fine and medium silt and <1% in coarse silt and fine clay. The more K_2O contents indicate the presence of weathering products of biotite

Table 3. *Elemental and mineral composition in selected fractions of silt and clay in semla series (Please explore a meaning in the fairly uniform depth distribution of Na_2O and CaO in the silt and clay fractions)*

Depth (cm)	Elemental composition (%)						Minerals (%)				feldspars		
	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	smectite	chlorite	mica	quartz	K	Na/Ca	zeolites
P1.Semla series –Aridic Haplusterts													
Coarse silt													
0-17	26.4	19.8	16.1	11.3	3.3	0.8	11	tr	3	6	8	54	15
17-42	13	13.4	5.6	5	1.9	0.5	7	tr	tr	5	13	70	4
42-57	10.9	12.6	5.1	4.7	1.7	0.4	3	1	tr	15	16	56	8
57-86	10	11.4	4.1	2.8	1.8	0.5	8	0	1	13	13	55	8
86-115	11	16.3	4.7	4.9	2	0.5	7	2	2	9	16	50	11
115-144	10.9	11.9	4.1	2.7	1.7	0.6	6	1	1	13	14	52	10
144-155	14	12.2	4.4	4.6	1.9	0.6	4	1	1	10	12	67	2
Medium silt													
0-17	14.9	9	3.4	3.3	2.6	0.7	15	tr	1	4	9	57	11
17-42	13.8	12.9	3.7	3.4	2.5	0.8	19	7	tr	5	8	58	3
42-57	14.4	13.6	3.7	3.2	2.7	0.8	14	5	tr	11	10	51	8
57-86	11.6	9.7	2.6	2	2.3	0.9	13	3	2	10	12	52	5
86-115	14.1	13.3	3.5	3.4	2.7	0.8	16	6	tr	12	9	48	7
115-144	10.6	10.9	3.1	2.7	2.2	1	18	3	4	10	8	47	1
144-155	14	11.9	2.8	3.9	2.3	0.9	15	1	2	8	7	60	3
Fine silt													
0-17	14.5	10.7	0.6	4.3	2	0.9	40	9	2	5	0	35	7
17-42	16.9	14.5	2	4.4	4.4	1.2	30	12	4	5	0	42	4
42-57	14.7	15.6	2.2	4.8	2.3	1	37	15	tr	9	0	31	3
57-86	13.2	12.5	1.3	3.5	1.8	1.3	37	11	4	11	0	22	4
86-115	15	14.8	4.3	6.3	2.4	1	34	11	1	8	0	33	2
115-144	13.1	11.5	1	3.4	2	1.3	28	5	3	11	3	35	2
144-155	15	13.6	0.9	5.1	1.2	0.8	38	4	1	4	0	42	3
Coarse +medium clay													
0-17	16.8	12.1	0	5.6	0.6	0.5	71.5	12	0.5	0	0	7.0	4.5
17-42	20.1	17.9	0.8	6.3	0.7	0.8	60.5	19	1.5	4.0	0	13.5	1.5

Table 3. *Continued ....*

Depth (cm)	Elemental composition (%)						Minerals (%)						
	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	smectite	chlorite	mica	quartz	feldspars		zeolites
											K	Na/Ca	
42-57	16.9	16.7	1.1	6.6	0.8	0.5	61	14.5	tr	5.0	0	14.0	2.0
57-86	18.2	16.2	0.5	5.8	0.6	1.4	58	9	4.5	5.0	0	8.5	4.0
86-115	17.6	17.7	1.4	7.7	0.8	0.6	64.5	13.0	1.0	3.0	0	6.5	2.0
115-144	17.6	17.1	2.4	7.5	0.6	1.3	62.5	9.0	5.0	2.5	0	11.5	1.5
144-155	15.8	13.6	0.1	4.6	0.2	0.3	72.5	1.0	tr	0	0	18.0	1.0
Fine clay													
0-17	15.6	10.9	0	3.6	0	0.3	99	0	1	0	0	0	tr
17-42	19.5	14.1	0	4.2	0.1	0.3	99	0	1	0	0	0	0
42-57	17.5	13.6	0.7	4.4	0.2	0.2	99	0	1	0	0	0	tr
57-86	16.4	13.9	0.1	3.9	0.2	0.5	99	0	1	0	0	0	0
86-115	16.5	13.7	0.4	4.8	0.4	0.1	99	0	1	0	0	0	0
115-144	16.2	15	0.6	4.4	0.2	0.5	99	tr	1	0	0	0	0
144-155	15.2	12	0.3	4.4	0.1	0.2	99	tr	1	0	0	0	0

and its strong association with silt plus clay fractions (Abdel Ghani, 1964).

The CIW(Maynard, 1992) in coarse and medium silt fractions showed high values 63 to 80 per cent in P2 as against P1 (50 to 68%) indicating more feldspar weathering in Sokhda series(P2). The bases to Al ratio and Ca to Al ratio's are generally high silt and clay fractions of Semla series (P1,Table 5) but relatively low K+Na to Al ratio(2.8 to 6.8 per cent). The salinization ratio(K+Na/Al*100) in silt fractions of Sokhda series (P2) is varied from 6.2 to 11.1 and is related with mean annual temperature. However, salinization is not reliable pedogenic process indicators because of differences in behaviour of K and Na and also Na less subject to diagenetic redistribution (Retallack, 1991). Using the regression equatons of Sheldon *et al.,* (2002) between mean annual temperature (MAT) and salinization of a Bw or Bss horizon: MAT(^{0}C) = “ 18.5S + 17.3 where the standard error (SE) is ±4.4°C, S is salinization. The underlying principle is that alkali elements (K and Na) are typically accumulated in desert settings, which usually have relatively low MAT (even if they are seasonally or daily high). Thus, high salinization ratios should have low MAT values. As per this equation , the differences in mean annual temperature of sokhada and semla series is almost 15±4.4. Further using CALMAG index (MAR=22.69*

Table 4. *Elemental composition and mineralogy of silt and clay fractions in sokhda series*

Depth(cm)	Elemental composition (%)						Minerals(%)				feldspars		
	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	smectite	chlorite	mica	quartz	K	Na/Ca	zeolites
P2.Sokhda series- Calcic Haplusterts													
Coarse silt													
0-11	7.8	8.2	1.7	1.9	1.3	0.7	tr	2	6	19	8	56	3
11-37	9.1	8.8	2.2	2.5	1.6	0.9	3	4	9	35	10	26	5
37-63	8.3	9.7	1.9	2	1.4	0.8	tr	0	9	25	33	23	5
63-98	9.5	10.3	1.9	2	1.7	1	3	2	2	17	25	45	4
98-145	8.6	10.8	1.8	2.1	1.4	0.9	0	2	5	14	18	53	5
145-160	5.6	1.7	0.8	0.2	1.2	0.9	0	2	13	19	30	32	2
Medium silt													
0-11	12.3	10.4	1.2	2.9	1.6	1.3	6	7	6	19	10	46	2
11-37	10.8	9.5	0.7	2.4	1.6	1.1	12	8	8	29	0	30	2
37-63	11.3	10.1	1	2.7	1.7	1.2	7	7	8	29	19	18	1
63-98	14.4	12	1.3	3.2	1.8	1.4	5	8	6	19	19	35	4
98-145	10.1	10.3	0.7	2.8	1.7	1.2	tr	8	9	20	15	38	4
145-160	9.7	3.7	0.5	1.1	1.5	1.5	0	7	13	21	22	27	3
Fine silt													
0-11	15.9	12.2	1.1	4.9	1.2	1.7	20	20	12	17	0	19	2
11-37	15.5	12.1	0.2	4.2	1.1	1.7	24	18	18	13	0	15	1
37-63	16	13.5	0.3	4.6	1	1.8	11	15	6	30	0	8	2
63-98	16.1	13.4	0.7	4.8	1.2	1.8	13	20	17	18	0	15	2
98-145	15.8	13.7	0.9	4.9	1.3	1.7	11	20	14	16	0	13	2
145-160	17.7	8.7	0.3	4.8	0.8	2.4	tr	22	24	16	14	14	4
Coarse +medium clay													
0-11	22.6	13.1	0	5.3	0.4	2	42.0	9.5	11.5	4.5	0	11.0	3.0
11-37	23.7	14.2	0.1	5.9	0.5	2.1	43.5	11.5	11.0	4	0	4.5	3.0
37-63	23.6	13.7	0.7	6.4	0.5	2.2	50.0	11.5	11.0	5	0	3.0	1.0
63-98	25.1	14.9	0	6.4	0.4	2.3	39.0	25.0	10.0	4	0	5.5	2.0
98-145	26.8	15.8	0.1	6.5	0.4	2.3	45.0	13.0	11.0	6	0	6.0	0.5
145-160	28.2	12.4	0.1	7	0.4	3.1	38.5	26.0	23.0	5	0	0	2.0

Table 4. *Continued ...*

Depth(cm)	Elemental composition (%)						Minerals(%)						
											feldspars		
	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	smectite	chlorite	mica	quartz	K	Na/Ca	zeolites
						Fine clay							
0-11	20.4	12.5	0	4.5	0	0.9	97	0	2	0	0	0	1
11-37	19.3	13	0	5	0.1	0.8	97	0	3	0	0	0	tr
37-63	18.1	12.4	0	4.6	0.1	0.7	95	0	5	0	0	0	tr
63-98	19.2	13.2	0	5.1	0.1	0.7	95	0	5	0	0	0	0
98-145	18.3	13.2	0	5.3	0.1	0.7	96	0	4	0	0	0	0
145-160	22.8	12.4	0	3.5	0.1	1.3	95	4	1	0	0	0	0

CALMAG-435.8, Nordt and Driesse, 2010) the mean annual rainfall (MAR) is estimated to be varying from 880mm to 960mm per year which slightly higher than the current rainfall in the region supporting the formation of smectite under humid past climate.

The smectite is more than 95 per cent in fine clay but only 3 per cent if coarse silt. The predominance of smectite over other mineral phases in the fine clay is the cause of shrink-swell properties in these soils. The CIA in coarse plus medium clay fractions of Sokhdad series(P2) is about 60 to 85 per cent as compared to Semla series (P1) with values of 45 to 59 per cent (Table 6). due to clay-rich in the first place with CIA values of 60 and above (Sheldon and Tabor , 2009). The weathering indices such as CIA is a measurement of the weathering of feldspar minerals and their hydration to form clay minerals. As clay content increases Al should also increase, whereas Ca, K, and Na contents should decrease, leading to higher CIA values. Further , the elemental composition of fine clay has a trend line of Al/Al+Fe versus Al/Al+Mg exceeding 0.5 suggesting a trend of in the direction of an iron analog of montmorillonite (Mermut, 1984, Table 6). The occurrence of iron rich smectites (propably iron rich bedillite) from basaltic parent rock (Krishnamurthi and Satyanarayana, 1969). The Fe-content of the smectite is a function of the chemical composition of the circulating water: nontronite is favoured by "dilute"neutral

Table 5. Molar ratios oxide concentrations of silt fractions

Soilseries	Coarse silt					Medium silt					Fine silt				
	CIA	CIW	Bases /Al	Ca/Al *100	K+Na/ Al*100	CIA	CIW	Bases/ Al	Ca/Al *100	K+Na/ Al*100	CIA	CIW	Bases/ Al	Ca/ *100	K+Na/ Al*100
P1. Semla series															
0-17	50.3	50.8	0.94	82.1	2.16	64.7	66.1	0.28	30.7	3.3	79.3	82.1	0.24	5.6	4.3
17-42	56.2	57.1	0.38	57.9	2.69	61.9	63.5	0.29	36.0	4.1	66.0	68.2	0.33	15.9	4.9
42-57	54.4	55.2	0.35	62.9	2.56	62.3	63.8	0.28	34.6	3.9	69.8	72.1	0.30	20.1	4.7
57-86	55.6	56.7	0.26	55.2	3.48	62.9	65.1	0.19	30.1	5.4	73.4	77.3	0.22	13.3	6.8
86-115	54.9	55.9	0.36	57.5	3.18	62.5	64.1	0.28	33.4	3.9	61.7	63.5	0.42	38.5	4.6
115-144	57.8	59.2	0.25	50.6	3.83	58.7	61.0	0.24	39.3	6.6	74.1	78.0	0.21	10.3	6.8
144-155	62.0	63.2	0.34	42.3	2.99	66.3	68.3	0.28	26.9	4.5	82.5	85.1	0.26	8.07	3.7
P2.Sokhda series															
0-11	64.5	67.2	0.15	29.3	6.2	73.6	77.8	0.18	13.1	7.3	79.6	84.6	0.26	9.3	7.4
11-37	62.5	65.3	0.19	32.5	6.8	75.1	79.2	0.15	8.7	7.0	85.0	90.8	0.20	1.7	7.6
37-63	63.6	66.4	0.16	30.8	6.6	73.0	77.1	0.17	11.9	7.3	85.0	91.0	0.22	2.5	7.8
63-98	64.4	67.6	0.16	26.9	7.3	74.8	78.8	0.20	12.1	6.7	81.7	87.2	0.24	5.8	7.7
98-145	64.7	67.8	0.16	28.1	7.2	72.8	77.4	0.17	9.3	8.2	80.1	85.2	0.25	7.6	7.5
145-160	64.3	69.2	0.05	19.2	11.1	73.6	79.9	0.09	6.9	10.7	85.5	92.9	0.22	2.2	9.4

systems and Mg-montmorillonite by concentrated, alkaline systems(Ghosh and Kapoor, 1982).

The first weathering products of plagioclase rich Deccan basalt is a dioctahedral smectite in arid to humid climate. Weathering of primary minerals contributes very little towards the formation of smectite. It is thus difficult to resolve the formation of large amounts of smectite clay in vertisols with the current semi arid climates. Therefore, smectites were formed in earlier humid climate and preserved in the nonleaching environment of arid and semiarid climate (Bhattacharyya *et al.*, 1993 and Pal *et al.,* 2009). At the high pH prevailing in the upper 54 cm of this soil (8.8-9), silica becomes most soluble and is free to recombine with soil cations such as Mg, Fe and Al to form secondary clay minerals.

Conclusions

Elemental composition and mineralogy of silt and clay fractions of typical moderately alkaline basaltic vertisols in semiarid (Semla series) and arid (Sokhada series) parts of Gujarat showed increase of clay content with concomitant increase of Al and decrease of Ca, K and Na contents. These vertic palesols have 45 to 60% clay, out of which 70 to 80 per cent is fine clay dominated by smectite and traces of mica. Elemental composition of these basaltic clay soils are rich in Mg and Fe with a significant differences in the ratio of bases

Table 6. *Molar ratios of geochemical elements in clay fractions*

Depth(cm)	Coarse plus medium clay					Fine clay	
	CIA	CIW	Bases/Al	Ca/Al *100	K+Na/ Al *100	Al/ Al+Fe	Al/Al+ Mg
			P1. Semla series				
0-17	55.5	95.9	0.80	0	2.11	0.87	0.77
17-42	55.0	91.4	0.82	5.35	2.76	0.87	0.78
42-57	49.3	87.5	1.03	8.76	2.06	0.87	0.76
57-86	54.5	92.9	0.84	3.69	5.32	0.86	0.77
86-115	46.4	86.2	1.15	10.71	2.36	0.87	0.74
115-144	45.0	81.7	1.22	18.36	5.11	0.86	0.76
144-155	59.4	97.7	0.68	0.85	1.31	0.87	0.74
			P2.Sokhda series				
0-11	62.4	97.9	0.60	0	6.11	0.82	0.67
11-37	60.8	97.0	0.64	0.57	6.12	0.81	0.63
37-63	57.8	93.9	0.73	3.99	6.44	0.81	0.64
63-98	60.7	98.2	0.65	0	6.33	0.81	0.63
98-145	61.7	97.8	0.62	0.50	5.93	0.80	0.61
145-160	60.7	97.9	0.65	0.48	7.59	0.84	0.75

to Al ratio, Ca to Al ratio and K+Na to Al ratio in both silt and clay fractions. Formation of smectites under humid past climate further confirmed with CALMAG index and molar ratio's of Na_2O and K_2O to Al_2O_3. The study of vertisols in semiarid and arid regions of Gujara suggested that geochemical records in relation to mineralogy is important to reconstruct climatic interpretation and the existence of iron rich smectites.

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Amorphous ferri-aluminosilicates in soils developed on different landforms in lower Brahmaputra valley of Assam

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Abstract : *Five soils developed on lower piedmont plain (P1: Ruptic-Ultic Dystrudepts), alluvial fan plain (P2: Aquic Udipsamments), alluvial plain (P3: Umbric Dystrudepts), flood plain (P4: Oxyaquic Udifluvents) and monadnock (P5: Typic Hapludults) in lower Brahmaputra valley zone of Assam were studied for amorphous ferri-aluminosilicates (AFAS). The amount of AFAS in clay fraction of soils varied from 10.1-38.1 per cent with SiO_2/Al_2O_3 ratio of 1.1-3.2and SiO_2/R_2O_3 ratio of 1.0-2.7. The highest amount of AFAS (30.7-38.2%) was found in soils developed on monadnock (P5) and the lowest amount (10.1-12.4%) in soils developed on piedmont plain (P1). The Bt horizons contained the highest amount of amorphous material within the profile. The major portion of AFAS was composed of tetrahedral $Si_3AlO_6(OH)_4$ component followed by octahedral $Al(OH)_{2.5}$ and FeOOH components. The hydroxyl water content of the amorphous material lies in the range of 16.4 to 21.1 per cent with an average of 18.5 per cent. The variation of hydroxyl water content was very narrow (18.1-18.4%) in more developed soils (Typic Hapludults) on monadnock.*

Key words : Amorphous material, ferri-alluminosilicate, tetrahedral, octahedral, hydroxyl water, biochemical weathering, humic acid, fulvic acid

Soils contain appreciable amount of free or combined oxides of Si, Al and Fe which are amorphous in nature and form important soil constituents influencing the physical and chemical properties of soils. The term 'allophane' has been used synonymously for the amorphous constituents which are generally amorphous hydrated aluminosilicates in the clay fraction of soils. Krishna Murti *et al.* (1976) reported that tropical ferruginous soils contained considerable iron in addition to silicon and aluminium and proposed a model for amorphous ferri-aluminosilicate (AFAS) consisting mainly of negatively charged tetrahedrally coordinated silica-alumina phase $Si_3AlO_6(OH)_4$ containing domains of neutral FeOOH, with an outer positively charged hydroxyaluminium polymeric component $[Al(OH)_{2.5}]_n$. Considerable amounts of amorphous materials were reported in clay fraction of laterite soils of Madhya Pradesh (Gaikwad and Govindarajan, 1971), in arid soils of Rajasthan (Choudhari and Dhir, 1983), in Vertisols (Seshagiri Rao *et al.*, 1992), in soils derived from mica-rich parent materials of Bihar (Mishra and Ghosh, 1994) and alluvium-derived soils of Assam (Karmakar and Borah, 1996). But the information on amorphous materials in soils developed on different landforms in high rainfall areas of Assam is lacking. In view of this, the present work was undertaken.

Materials and Methods

The study area is situated between 26°07' N and 26°42' N latitudes and 89°58' E and 90°20' E longitudes in the lower Brahmaputra valley of Assam. The area is characterized by humid sub-tropical climate with mean annual rainfall of 2733 mm and mean annual temperature of 24.6°C with hot and wet summer and dry and cool winter. The soil-moisture and temperature regimes of the area are *udic* and *hyperthermic,* respectively.

Five soil profiles collected from different physiographic units namely, lower piedmont plain (Kochugaon, P1: Ruptic-Ultic Dystrudepts), alluvial fan plain (Gossaigaon, P2: Aquic Udipsamments), alluvial plain (Bhaoraguri, P3: Umbric Dystrudepts), flood plain (Khoraghat, P4: Oxyaquic Udifluvents) and monadnock (Alamganj, P5: Typic Hapludults), within a transect of lower Brahmaputra valley zone of Assam, were studied in the present investigation. The soils on these physiographic units are at varying degree of development stage as indicated by Soil Taxonomy (Karmakar and Rao, 1999a) and are developed from sedimentary and partially metamorphosed rocks as indicated by fine sand mineralogy (Karmakar and Rao, 1999b). Kaolinite and illite are the dominant clay minerals in these soils (Karmakar and Rao, 1998).

Horizon-wise soil samples were analysed for physical and chemical properties (Jackson, 1973), exchangeable acidity (Peech, 1965) and dithionite-extractable iron (Mehra and Jackson, 1960; Krishna Murti *et al.,* 1970). Clay was separated after removal of organic matter, free iron and aluminium oxides (Jackson, 1956). The amorphous material in the clay fraction was extracted by selective dissolution method (Hashimoto and Jackson, 1960) by flash boiling 100 mg of Na-saturated clay with 100 ml of 0.5 N NaOH for 2.5 minutes. The extract was centrifused and Si was determined by molybdate yellow colour method (Jackson, 1973) and Al by aluminon method (Krishna Murti *et al.*, 1974). The iron in the residue clay was extracted by dithionite-citrate-bicarbonate method (Mehra and Jackson, 1960) and determined colorimetrically (Krishna Murti *et al.*, 1970). Ignited soil samples were analysed for total elemental composition (Jackson, 1973). Weathering indices of the soils were determined using the formulae of (i) Evans and Cameron (1979): WI_{EC} = Molar ($CaO + MgO + K_2O + Na_2O$) / Molar ($CaO + MgO + K_2O + Na_2O + SiO_2 + Al_2O_3 + Fe_2O_3$) expressed in percent and (ii) Torrent (1980): $WI_T = Fe_d$ /

Fe_t. The WI_{EC} decreased with increasing soil age as more mobile elements are lost. On the other hand, WI_T increased with soil age. In the present investigation, there was a significant negative correlation (r = -0.792**) between WI_{EC} and WI_T.

The amount of amorphous materials was calculated by adding the amount of SiO_2, Al_2O_3, Fe_2O_3 and calculated hydroxyl water content obtained by using the model of Krishna Murti *et al.* (1976).

Results and Discussion

The soils varied considerably in the physical and chemical properties (Table 1). The soils on monadnock (P5) contained the

Table 1. *Physical and chemical properties of soils*

Horizon	Depth (cm)	Sand	Silt	Clay	Org. matter %	pH	Exch. acidity cmol(p^+) kg^{-1}	CEC	WI_{EC} %	WI_T	Clay CEC cmol(p^+) kg^{-1} clay
		←	%	→							
P1: Lower piedmont plain (Kochugaon) : Ruptic-Ultic Dystrudept											
A	0-9	33.2	34.9	31.9	6.3	5.7	16.5	27.9	4.76	0.33	25.4
BA	9-23	31.8	32.4	35.8	3.5	5.4	20.2	23.3	3.45	0.43	28.0
Bt	23-37	28.4	30.5	41.1	2.7	4.8	18.8	20.4	3.30	0.42	26.6
BC	37-100+	35.5	27.9	36.6	0.8	5.1	9.8	10.9	3.69	0.41	24.6
P2: Alluvial fan plain (Gossaigaon): Aquic Udipsamment											
Ap	0-20	68.7	18.7	12.6	1.6	5.6	9.1	10.7	4.61	0.13	28.6
AC	20-33	75.5	13.9	10.6	0.8	5.6	5.0	7.7	4.64	0.11	31.3
C1	33-46	86.2	5.2	8.6	0.3	5.8	1.8	4.8	4.22	0.07	29.0
P3: Alluvial plain (Bhaoraguri) : Umbric Dystrudept											
A1	0-6	38.2	32.8	29.0	5.3	5.1	16.1	22.4	4.26	0.19	28.0
A2	6-18	39.7	33.1	27.2	4.6	5.2	18.0	20.2	3.93	0.18	31.3
Bw	18-63	35.2	42.3	22.5	0.8	5.7	7.4	10.5	5.47	0.18	22.1
2C1	63-103	79.3	7.2	13.5	0.2	5.7	3.7	6.0	4.22	0.12	23.8
2C2	103-130	85.2	6.9	7.9	0.1	5.9	1.3	5.1	4.43	0.12	26.6
P4 : Flood plain (Khoraghat) : Oxyaquic Udifluvent											
A1	0-6	34.5	31.2	34.3	2.5	5.7	10.2	14.4	4.81	0.21	20.9
A2	6-18	28.7	35.9	35.4	2.2	5.6	11.1	13.7	5.03	0.21	17.2
2C1	18-46	52.8	31.8	15.4	0.6	5.6	6.2	7.6	5.36	0.18	15.2
2C2	46-146	63.0	24.2	12.8	04	5.8	4.1	5.0	6.17	0.15	18.4
3C3	146-167	65.7	16.8	17.5	0.1	6.1	2.1	3.4	5.09	0.13	19.0
P5 : Monadnock (Alamganj) : Typic Hapludult											
Ap	0-14	43.5	25.9	30.6	2.1	5.2	15.2	16.8	2.85	0.50	31.4
BA	14-31	38.3	25.4	36.3	1.5	4.8	13.9	15.9	2.52	0.56	30.5
Bt1	31-53	23.0	25.5	51.5	1.0	4.9	15.1	19.5	2.73	0.42	38.0
Bt2	53-130+	25.8	26.7	47.5	0.6	5.0	14.6	16.1	2.89	0.50	35.2

highest amount of clay (30.6-51.5 per cent) followed by that on piedmont plain (P1). The soils on alluvial fan plain (P2), alluvial plain (P3) and flood plain (P4) showed decreasing trend of clay distribution with soil depth. The soils on lower piedmont plain contained the highest amount of organic matter (0.8 – 6.3 %). The pH of the soil was in the acidic range (4.8-6.1) and CEC varied from 14.4 – 27.9 cmol(p^+) kg^{-1} in the surface and 3.4 – 23.3 cmol(p^+) kg^{-1} in the subsurface. The soils exhibited considerable amount of exchangeable acidity varying from 9.1 – 16.1 cmol(p^+) kg^{-1} in the surface and 1.8 – 20.2 cmol(p^+) kg^{-1} in the subsurface. The lowest value of WI_{EC} and the highest value of WI_T in the soils on monadnock (P5) indicate that these soils are well developed (Typic Hapludults) followed by those on piedmont plain (P1) which are moderately developed (Ruptic-Ultic Dystrudepts).

The constituents of amorphous materials in the clay fraction of soils (Table 2) showed higher amount of SiO_2 (3.9-17.2 %) and Al_2O_3 (3.0-12.0%) than Fe_2O_3 (0.8-2.1%). Similar findings were reported earlier for some soils of Assam (Das and Sharma, 1980; Karmakar and Bora, 1996). Presence of substantial amount of Fe_2O_3 in the amorphous materials is corroborated by strong to very strong exothermic peak at 310-331 °C in the DTA curve of soil clays (Karmakar and Rao, 1998). The strong exothermic peak in the 250-500 °C may be due to the crystallization of virtually amorphous ferric oxides to hematite (MacKenzie, 1949, Mitchell, 1953). Mitchell and Farmer (1962) also observed that amorphous hydrated ferric oxide precipitates exhibit exothermic peaks between 300-500 °C. The well developed soils on monadnock (P5: Typic Hapludults) contained the highest amounts of SiO_2 (14.5-17.1%), Al_2O_3 (9.2-12.0%) and Fe_2O_3 (1.4-2.1%) with increasing trend in soil depth as compared to Inceptisols developed on piedmont plain (P1), alluvial plain (P3) and Entisols developed on alluvial fan plain (P2) and flood plain (P4). This finding clearly indicates that more amounts of amorphous SiO_2, Al_2O_3 and Fe_2O_3 are formed with advanced stage of soil development in acidic soil environment under humid subtropical climatic condition. This is corroborated by a negative correlation of SiO_2, Al_2O_3 and Fe_2O_3 with pH and WI_{EC} and a positive correlation with WI_T (Table 4). MacKenzie *et al.* (1962) observed that a higher pH favours the crystallization of synthetic amorphous alumina.

Molar SiO_2 / Al_2O_3 ratio (1.1-3.2) and SiO_2 / R_2O_3 ratio (1.0-2.7) suggest that the amorphous materials of the studied soils were siliceous in nature. Higher SiO_2 / Al_2O_3 ratio (3.1-3.8) and SiO_2 / R_2O_3 ratio (2.7-3.0) observed in the A-horizons of P2 (Aquic Udispamments) and P4 (Oxyaquic Udifluvents) might be due to high organic matter content and periodical water saturation in these soils. Similar findings

Table 2. *Constituents of amorphous materials extracted from soil clays by 0.5 N NaOH followed by CBD treatment*

Horizon	Depth (cm)	SiO_2	Al_2O_3	Fe_2O_3	Molar SiO_2/Al_2O_3	Molar SiO_2/R_2O_3
		←	% →	(%)		
P1: Lower piedmont plain (Kochugaon) : Ruptic-Ultic Dystrudept						
A	0-9	4.15	3.02	1.16	2.33	1.87
BA	9-23	4.37	3.34	1.11	2.20	1.83
Bt	23-37	4.64	4.13	1.32	1.90	1.50
BC	37-100+	4.19	4.29	1.13	1.65	1.41
P2: Alluvial fan plain (Gossaigaon): Aquic Udipsamment						
Ap	0-20	6.61	2.99	1.20	3.78	2.99
AC	20-33	5.37	3.18	1.41	2.87	2.23
C1	33-46	5.12	3.02	2.72	2.88	1.83
P3: Alluvial plain (Bhaoraguri) : Umbric Dystrudept						
A1	0-6	6.51	5.12	1.25	2.16	1.87
A2	6-18	6.16	5.09	1.41	2.05	1.75
Bw	18-63	4.52	6.20	0.97	1.24	1.12
2C1	63-103	6.61	10.65	1.14	1.05	0.99
2C2	103-130	5.69	7.79	1.54	1.24	1.10
P4 : Flood plain (Khoraghat) : Oxyaquic Udifluvent						
A1	0-6	6.04	3.05	0.84	3.10	2.69
A2	6-18	5.97	3.18	0.91	3.18	2.69
2C1	18-46	3.92	5.09	1.36	1.31	1.12
2C2	46-146	5.29	5.57	0.97	1.61	1.45
3C3	146-167	6.76	6.36	1.59	1.80	1.56
P5 : Monadnock (Alamganj) : Typic Hapludult						
Ap	0-14	14.51	9.22	1.38	2.67	2.44
BA	14-31	15.67	10.81	1.48	2.47	2.26
Bt1	31-53	17.29	11.93	1.97	2.46	2.23
Bt2	53-130+	17.08	11.96	2.06	2.42	2.18

were also reported by Karmakar and Borah (1996) in some Inceptisols of Assam. This is also supported by a positive correlation of organic matter with SiO_2/Al_2O_3 (r= 0.228) and SiO_2/R_2O_3 (r= 0.243).

The Si, Al and Fe extracted by 0.5N NaOH and subsequent CBD treatment were allocated to the three components as envisaged in the model of Krishna Murti *et al* (1976). All the iron was taken to constitute the FeOOH component. All the Si was assigned to the tetrahedral core with sufficient Al to give the cationic content of $Si_3AlO_6(OH)_4$. The remaining Al was assigned to octahedrally coordinated Al polymer of empirical formula $Al(OH)_{2.5}$. As the iron in the amorphous material was

Table 3. *Amorphous ferri-aluminosilicate and its structural components in soil clay*

Horizon	Neutral FeOOH	Tetrahedral $Si_3AlO_6(OH)_4$	Octahedral $Al(OH)_{2.5}$	Hydroxyl water	Amorphous material	Tetrahedral Octahedral Component
			$\longleftarrow \% \longrightarrow$			
P1: Lower piedmont plain (Kochugaon) : Ruptic-Ultic Dystrudept						
A	1.29 (12.72)	6.33 (62.43)	2.52 (24.85)	1.81 (17.85)	10.14	2.51
BA	1.23 (11.41)	6.67 (61.87)	2.88 (26.72)	1.96 (18.18)	10.78	2.32
Bt	1.47 (11.86)	7.08 (57.14)	3.84 (30.99)	2.30 (18.56)	12.39	1.84
BC	1.26 (10.61)	6.40 (53.87)	4.22 (35.52)	2.27 (19.11)	11.88	1.52
P2: Alluvial fan plain (Gossaigaon): Aquic Udipsamment						
Ap	1.33 (10.28)	10.09 (77.97)	1.52 (11.75)	2.14 (16.54)	12.94	6.64
AC	1.57 (13.04)	8.20 (68.11)	2.27 (18.85)	2.08 (17.27)	12.04	3.61
C1	3.03 (23.32	7.82 (60.20)	2.14 (16.47)	2.13 (16.40)	12.99	3.65
P3: Alluvial plain (Bhaoraguri) : Umbric Dystrudept						
A1	1.39 (8.79)	9.94 (62.87)	4.48 (28.34)	2.93 (18.53)	15.81	2.22
A2	1.57 (10.11)	9.40 (60.53)	4.56 (29.36)	2.87 (18.48)	15.53	2.06
Bw	1.08 (7.36)	6.90 (47.00)	6.70 (45.64)	2.99 (20.37)	14.68	1.03
2C1	1.27 (5.45)	10.09 (43.29)	11.95 (51.26)	4.91 (21.06)	23.31	0.84
2C2	1.71 (9.08)	8.69 (46.17)	8.42 (44.74)	3.80 (20.19)	18.82	1.03
P4 : Flood plain (Khoraghat) : Oxyaquic Udifluvent						
A1	0.93 (7.16)	9.77 (75.21)	2.29 (17.63)	2.25 (17.32)	12.99	4.27
A2	1.01 (8.31)	9.11 (74.98)	2.03 (16.71)	2.09 (17.20)	12.15	4.49
2C1	1.51 (11.70)	5.98 (46.36)	5.41 (41.94)	2.53 (19.61)	12.90	1.10
2C2	1.08 (7.34)	8.07 (54.86)	5.56 (37.80)	2.88 (19.58)	14.71	1.45
3C3	1.77 (9.76)	10.32 (56.89)	6.05 (33.35)	3.43 (18.91)	18.14	1.71
P5 : Monadnock (Alamganj) : Typic Hapludult						
Ap	1.54 (5.02)	22.15 (72.22)	6.98 (22.76)	5.56 (18.13)	30.67	3.17
BA	1.65(4.81)	23.92 (69.78)	8.71 (25.41)	6.32 (18.44)	34.28	2.75
Bt1	2.19 (5.74)	26.39 (69.16)	9.58 (25.10)	6.97 (18.26)	38.16	2.75
Bt2	2.29 (6.01)	26.07 (68.42)	9.74 (25.56)	7.00 (18.37)	38.10	2.68

Figures in the parentheses represent the per cent constituents of amorphous ferri-aluminosilicate

extracted by CBD only after the 0.5N NaOH treatment, it was believed to form a separate phase as small neutral domains within the negatively charged Al-Si tetrahedrally coordinated core having a positively charged outer octahedrally coordinated hydroxyaluminium polymer. Rich (1968) also suggested that occlusion of $Fe(OH)_3$ in positively charged hydroxyl-aluminum interlayers appear to be more likely. The amount of amorphous materials was calculated by adding the amount of

SiO_2, Al_2O_3, Fe_2O_3 and calculated hydroxyl water content obtained from this model. The amount of amorphous material may also be obtained by sum of the amount of FeOOH, $Si_3AlO_6(OH)_4$ and $Al(OH)_{2.5}$.

The amorphous materials in the studied soils (Table 3) varied from 10.1 – 38.1 per cent. The lowest amount (10.1 – 12.4%) was found in the soils of P1 (Ruptic-Ultic Dystrudepts) on piedmont plain and the highest amount (30.6 – 38.2 was found in the soil of P5 (Typic Hapludults) on monadnock showing an apparent increasing depth-distribution. It is note-worthy that the Bt horizons contained the highest amount of amorphous material within the profile. The significant correlation of amorphous material with weathering indices (Table 4) indicates that more amount of amorphous material was produced with soil development, which was favoured by acidic environment as is evident from significant negative correlation coefficient between amorphous material and pH (r= – 0.500**).

The composition of amorphous material (Table 3) showed that the major portion of the amorphous material was composed of tetrahedral $Si_3AlO_6(OH)_4$ component (43.3 – 78.0 %) followed by octahedral $Al(OH)_{2.5}$ component (11.8– 51.3 %) and neutral FeOOH component (4.8 – 23.3%). Karmakar and Borah (1996) also reported similar findings for some Inceptisols of Assam. The surface horizons contained higher amount of tetrahedral component with decreasing trend in soil depth whereas a reverse trend was observed in case of octahedral component. The tetrahedral component, as well as the ratio of tetrahedral/octahedral component, was also higher in A-horizons containing higher amount of organic matter. This may be due to more biochemical weathering in the A-horizons in presence of high organic matter. A significant negative correlation coefficient (r= –0.564*) with pH indicates that more amount of tetrahedral $Si_3AlO_6(OH)_4$ is formed with increasing soil acidity. Significant correlation coefficients of tetrahedral components with weathering indices (Table 4) suggest that more amount of tetrahedral $Si_3AlO_6(OH)_4$ is formed with advanced stage of soil development in the studied soils. The distribution of FeOOH did not show any regular pattern with soil depth. This may be due to the fact that the precipitation of iron is mainly related to redox condition which in turn is related to drainage (in case of P1, P5) and fluctuating ground water (in case of other soils). The hydroxyl water content of the amorphous material (Table 3), calculated from the structural model, lies in the range of 16.4 to 21.1 per cent with an average of 18.5 per cent which is closer to values of 17.8 percent calculated by Krishna Murti *et al.* (1976) and of 19.0 per cent obtained by Das and Sharma (1980) and Karmakar and Borah (1996). It is note-worthy that the variation of hydroxyl water content in amorphous material was more (16.4-21.1 percent) in less developed soils (Entisols and Inceptisols), whereas it was very narrow (18.1 – 18.4 per cent) in more developed soils (Typic Hapludults). Significant correlation coefficients (Table 4) indicate that hydroxyl water content of amorphous material is related to soil acidity and weathering intensity.

Genesis of amorphous materials

The soils were developed on parent materials derived from sedimentary and partially metamorphosed rocks as indicated by fine sand mineralogy showing dominance of quartz (41.0 – 61.3%), orthoclase (27.6 – 39.2%), plagioclase (1.8 – 6.3%) and muscovite (9.3 – 25.8%) in the light fraction and zircon (19.0 – 34.3%), biotite (23.2 – 29.3%), chlorite (19.6 – 31.4%), hypersthene (0-8%) and kyanite (2.2 – 7.2%) in the heavy fraction (Karmakar and Rao, 1999b). Kaolinite and illite are the dominant clay minerals in these soils (Karmakar and Rao, 1998). Weathering of primary minerals particularly hydrolysis of feldspars and acid weathering of mica minerals under humid sub-tropical climatic condition might have released the constituents (Si, Al, Fe) resulting the formation of amorphous materials and then kaolinite. The significant negative correlation coefficient (r = – 0.918**) between clay and sand reflects the neosynthesis of clay in these soils. The neosynthesis of kaolinite *via* amorphous ferri-aluminosilicates from the hydrolysis of primary minerals is possible under humid sub-tropical climate where intense leaching of bases due to high rainfall has resulted in soil acidity which is conducive for the formation of kaolinite. This hypothesis holds well because the breaking of kaolinite in the high rainfall is improbable (Singer, 1966).

Table 4. *Correlation coefficients among constituents of amorphous material and important soil parameters*

	Sand	Silt	Clay	OM	pH	CEC	Exch. Acidity	WI_{EC}	WI_T
SiO_2	-0.318	-0.042	0.539*	-0.165	-0.566*	0.208	0.294	-0.705**	0.634**
Al_2O_3	-0.103	-0.189	0.310	-0.364	-0.385	-0.035	0.035	-0.537**	0.441*
Fe_2O_3	0.263	-0.513	-0.016	-0.303	-0.129	-0.157	-0.155	-0.411	0.067
SiO_2/Al_2O_3	-0.123	0.013	0.188	0.228	-0.122	0.242	0.246	-0.195	0.101
SiO_2/R_2O_3	-0.271	0.128	0.333	0.243	-0.223	0.317	0.343	-0.269	0.263
Clay CEC	-	-	0.389	0.132	-0.606**	0.412	0.441*	-0.789**	0.466*
FeOOH	0.263	-0.514*	-0.016	-0.304	-0.130	-0.157	-0.155	-0.412	0.068
$Si_3AlO_6(OH)_4$	-0.321	-0.040	0.542*	-0.164	-0.564**	0.209	0.294	-0.704**	0.633**
$Al(OH)_{2.5}$	0.029	-0.239	0.141	-0.420	-0.223	-0.166	-0.117	-0.359	0.266
Hydroxyl water	-0.182	-0.153	0.409	-0.309	-0.467*	0.051	0.128	-0.628**	0.530*
AFAS	-0.215	-0.136	0.449*	-0.277	-0.500*	0.092	0.172	-0.664**	0.563**
Tetrahedral Octahedral	-0.014	-0.043	0.056	0.141	-0.014	0.121	0.129	-0.082	-0.027

Table 5. *Correlation coefficients among components of amorphous material*

	FeOOH	$Si_3AlO_6(OH)_4$	$Al(OH)_{2.5}$	Hydroxyl water	AFAS
$Si_3AlO_6(OH)_4$	0.412	1.000			
$Al(OH)_{2.5}$	0.210	0.598**	1.000		
Hydroxyl water	0.390	0.927**	0.854**	1.000	
AFAS	0.430*	0.964**	0.786**	0.993**	1.000
Tetrahedral Octahedral	0.051	0.161	-0.548*	-0.153	-0.058

The soils contained appreciable amount of humus consisting of 10.0-52.4% humic acid and 47.6-90.0% fulvic acid carbon (Karmakar and Rao, 1999c). Biochemical weathering in presence of these organic acids might have also led to the destruction of primary minerals. Tan (1980) observed that humic acid and fulvic acid disintegrate microcline, biotite and muscovite. However, fulvic acid extracted ten times more silica and six times more aluminium at pH 2.5 than at pH 7.0. Linares and Huertas (1971) observed that the presence of fulvic acid led to the formation of kaolinite from solutions that contained Si and Al. The same mechanism might be assumed to be in operation in the studied soils because the major portion of humus was fulvic acid. A considerable amount of iron present in the amorphous material of CBD pre-treated clay fraction suggests that iron is a structural component in the amorphous material as well as in the kaolinite. Das (1977) found a positive correlation between iron content in kaolinite and iron content in amorphous materials in some soils of Assam. So the amorphous materials may be regarded as amorphous ferri-aluminosilicates (AFAS). The higher amount of AFAS in the soils on monadnock (P5: Typic Hapludults) suggests that the rate of recombination of hydrolytic products is slower than the rate of hydrolysis of primary minerals.

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Linking Minerals to Selected Soil Bulk Properties and Climate Change: A Review

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Abstract : *Reviews in the past on the significance of minerals indicated that despite our best management interventions the actual agricultural productivity does vary because factors beyond our control. One intrinsic factor in yield variation is soil type and clay is an important soil constituent that controls many properties. There is ample evidence to show that the amount and type of clay in a soil has a very important bearing on the genesis, characteristics, and physical and chemical properties and nutrient dynamics in soil plant continuum of soils. However, information with regard to significance that clay and other soil minerals have in major bulk properties of soils (edaphology) and in finding signatures of climate change in soils/sediments of the past (paleopedology) has been rare. A search for links between mineralogy and soil properties of agricultural importance and use of minerals in unravelling the climate of the past often poses problems because descriptions of soil minerals are inadequate or incomplete. This becomes more difficult as soil minerals do not remain as specimen minerals in soil environment. An endeavour made at NBSS&LUP in 2000 indicated that first hurdle lies in proper identification, let alone quantitative estimation, of soil clays and other minerals. However, through sustained efforts by the researchers at NBSS & LUP (ICAR) since then, further advances in knowledge has been possible and this demands for another critical review. Thus, this review is the synthesis of the updated knowledge, which has come out as state of the art information that will fulfill the need of a hand book to facilitate their better management for optimizing their productivity in the 21st Century even amidst the climatic adversities due to climate change.*

Minerals in soils are the result of both inheritance and authigenic formation of both primary and secondary minerals. Comprehensive reviews on the soil clay minerals and other minerals in the past indicate that there are not many attempts to show the influence of minerals in soil genesis and management (Mukherjee *et al*., 1971; Raman and Ghosh, 1974; Ghosh and Kapoor, 1982; Sarma and Sidhu, 1982; Ghosh and Bhattacharyya, 1983; Ghosh, 1997). A review in the past on this subject and related issues (Newman, 1984; Ghosh, 1997; Wilson, 1999) pointed out that the increase in agricultural productivity during the middle of the twentieth century was due to human influence, which improved vastly the soil fertility on all types of soil. However, actual productivity does vary widely and this fact shows that there are other factors of productivity beyond our control. One intrinsic factor in yield variation is soil type, which is related to the soil composition and its position in the landscape. Clay is an important soil constituent controlling its properties. Despite the fact that there is ample evidence to show that the amount of clay in a soil has a very important bearing on the genesis, characteristics, and physical and chemical properties of soils, it would be more appropriate to see what significance clay mineral *type* and other soil minerals have in soils; pedology, paleopedology, polygenesis and edaphology in particular. A search for links between mineralogy and soil properties of agricultural importance is likely to be difficult because many a time the description of minerals actually present in a soil is inadequate or incomplete. Further, as soil minerals often differ from "type" minerals, it is very much necessary to investigate the properties of these minerals relevant to the properties of the soil in bulk. In this endeavour, Pal *et al.* (2000a) demonstrated a good number of examples that indicated despite soil clay minerals being a mixture of several components, adequate description is possible. However, for the last decade some more information on this important area of soil research including the use of clay mineral as proxy to the climate change phenomena in the Peninsular and extra – Peninsular areas, has been generated at national level, specially at the National Bureau of Soil Survey and Land Use Planning (NBSS&LUP)(ICAR). Through synthesis of the present dataset on the nature and characteristics of primary and secondary minerals of Indian soils, this review as a state-of-the-art information is made, which has established a link between minerals and selected bulk soil properties and also climate change. It is hoped that this review will fulfil the need of a hand book for students and young researchers in earth science who would intend to assess the health and quality of soils while developing suitable management practices to enhance and sustain their productivity in the 21st Century.

Characteristics and nature of clay minerals in adsorption and desorption of major nutrients

Nitrogen adsorption and clay minerals

Increasing demand for nitrogen fertilizers to produce food has always stimulated research to gain knowledge on the various forms of nitrogen in soils. One of the forms of nitrogen (N) is the fixed NH_4-N. Despite many tropical soils being endowed with large amounts of fixed ammonium (Dalal, 1977), information on this important form of N is rare, especially in the semi-arid tropical (SAT) soils

(Burford and Sahrawat, 1989). Sahrawat (1995) determined the fixed NH_4-N distribution in two of the benchmark (BM) Vertisols of Indian SAT, namely Kasireddipalli soils at ICRISAT Center, Patancheru and Barsi soils of Maharashtra state of western India. They reported that the amount of fixed NH_4-N was 22 to 59% in the former and 16 to 31% in the latter in the total soil N. The 2:1 non- expanding minerals like vermiculites can only fix NH_4-N. Despite this knowledge, illites (micas) and smectites are considered as the minerals to fix NH_4-N (Nommik and Vahtras, 1982). Smectites do not have any selectivity for non-hydrated monovalent cation like K because of their low layer charge (Brindley, 1966). The NH_4 ion being also a non-hydrated monovalent cation having almost the same ionic radii as that of K is not expected to be fixed in the interlayers of smectites. Similarly, it is difficult to understand the NH_4 ion fixing capacity of illites because illites do not expand when saturated with divalent cations (Sarma, 1976). Vertisols developed in the basaltic alluvium of the Deccan basalt of Peninsular India, are not devoid of vermiculite as reported (Mengel and Busch, 1982; Dhillon and Dhillon, 1991). However, the identification of vermiculite by XRD analysis in different soil size fractions is fraught with some difficulty in ubiquitous presence of chlorite and also because of its presence in small amounts in Vertisols and other soil types. Its presence is resolved by following the progressive reinforcement of the 1.0 nm peak of mica while heating the K-saturated samples at 25, 110, 300 and 550°C (Fig.1) (Pal and Deshpande, 1987a;

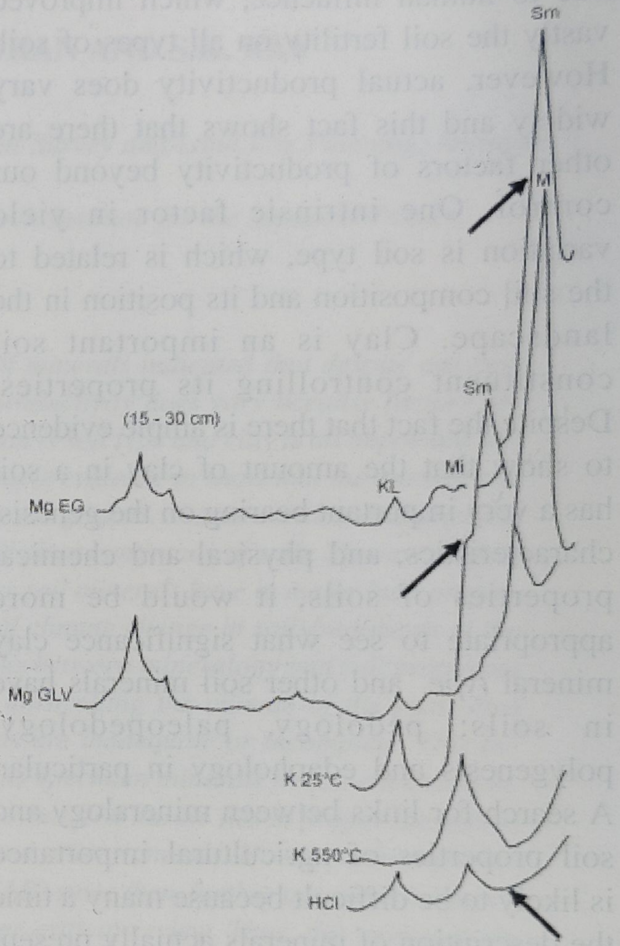


Fig. 1. *Representative XRD diagram of fine clay (< 0.2µm) fraction of Vertisols. On glycolation it expands to 1.7 nm indicating the dominant presence of smectite (Sm). With glycerol vapour treatment it expands to about 1.8 nm, indicating that the smectite is nearer to montmorillonite. On K-saturation, its 1.0 nm region gets reinforced, indicating the presence of small amount of vermiculite which is not detected on glycolation. Adapted from Pal and Durge (1989).*

Pal and Durge, 1987), and it is estimated semi-quantitatively following the method of Gjems (1967). Like other soil types, Vertisols do contain vermiculite in their silt (50-2μm), coarse clay (2-0.2μm) and fine clay (<0.2μm) fractions (Pal and Durge, 1987) and the content of vermiculite, determined quantitatively (Alexiades and Jackson, 1965) ranges from 2.0 to 3.5% in the silt, 3.5 to 10% in the coarse clay and 5.0 to 9.5 % in the fine clay fractions (Pal and Durge, 1987). Vermiculite is trioctahedral in nature, and is the alteration product of biotite in the presence of its dioctahedral variety (muscovite) (Pal and Durge, 1987; Pal *et al*., 2001a). Both the micas are not part of the Deccan basalt and their origin in Vertisols has been attributed to the geomorphic history of the Deccan basalt landscape areas (Pal and Deshpande, 1987a). Thus, it would be prudent to attribute the observed N fixation in Vertisols (Sahrawat, 1995) and other soil as $NH4^+$, to the presence of vermiculite. Such basic understanding is essential to include fixed NH_4-N in assessing the potentiality of N availability in Indian soils.

Phosphorous (P) adsorption and clay minerals

Soil properties that are linked to P adsorption by soil minerals include the nature and amount of clay, organic matter, and hydrous oxides of iron and aluminium (Sanyal and De Datta, 1991). Based on earlier findings these authors indicated a significant correlation of P sorption parameters with clay content and opined that this may be a mere reflection of the effect of specific surface area on P adsorption.

Clays rich in 1:1 lattice mineral may contribute to P adsorption in highly weathered soils of humid tropical climate, especially at low soil pH, when the activity of iron and aluminium is also expected to be higher. Thus, the free hydrated oxides of iron and aluminium ordinarily present in ferruginous soils have considerable phosphate fixing ability (Biddappa and Venkat Rao, 1973). Kanwar and Grewal (1960) also reported that about 70 per cent of the phosphate fixing capacity of acid soils and 30 per cent of that of calcareous and alkali soils of Punjab were due to free sesquioxides. In soils hydrous oxides of iron and aluminium occur as fine coatings on surfaces of clay minerals (Greenland *et al*., 1968; Haynes, 1983). These coatings having appreciably large specific surface area can adsorb large amounts of added P. This observation clearly implies that in P adsorption crystalline aluminosilicate minerals have a merely secondary role (Ryden and Pratt, 1980). However, hydroxides of iron and aluminium can adsorb negatively charged phosphate ions only when they remain as cations in highly acidic medium. Such soils (Ultisols) are highly acidic and their KCl pH values remain close to or greater than water pH (Bhattacharyya *et al*., 2000; Chandran *et al*., 2005), indicating the presence of gibbsite and/or amorphous materials (Smith, 1986). A negative/zero/positive ÄpH indicates the presence of variable charge minerals such as gibbsite and /or sesquioxides (Uehera and Gillman, 1980; Bhattacharyya *et al.*, 1994). This indicates that gibbsite and /or sesquioxides in acidic soils showing a positive ΔpH could be a better substrate to absorb negatively charged phosphate ions. Therefore, reported adsorption of added phosphate ions by soils of the semi-arid and arid climates is difficult to reconcile since the soils in these regions are alkaline and sodic due to the formation of pedogenic $CaCO_3$ (Pal *et al.*, 2000b, 2009). In such pedo-environment layer silicates suffer congruent dissolution (Pal, 1985). This suggests that the highest surface area of 2:1 expanding clay minerals and/or hydroxides of iron and aluminium with no positive sites, have little role in the adsorption of added negatively charged phosphate ions in calcareous and mild to moderately alkaline soils. This supports the ICRISAT's classical experimental observations that P adsorption and desorption is not a major problem in Vertisols, and that all the adsorbed P is easily exchangeable by P^{32} and little amount of P is adsorbed in the non-exchangeable form (ICRISAT, 1988; Sahrawat and Warren, 1989; Shailaja and Sahrawat, 1990, 1994; Warren and Sahrawat, 1993).

Potassium release and biotite mica

The prime K-bearing minerals in major soils (alluvial, black and ferruginous soils) of India are micas that are concentrated mainly in the silt and clay fractions. Despite this favourable natural mineral endowment, crop response to K fertilizers in many such soils has been anomalous (Pal *et al.*, 2000a, 2001a; Pal, 2003). Petrographic examination of sand fractions of major soils of India confirmed the presence of muscovite and biotite in soils of the Brahmaputra alluvium (BA) and Indo-Gangetic alluvium (IGP) and also in black soils. Muscovite particles were very rare in ferruginous soils. In soils of IGP and BA, muscovite was more common than biotite. In black soils amounts of micas were low as compared to the other two soils and biotite was more common than muscovite (Pal *et al.*, 2001a). SEM examination of micas by Pal *et al.* (2000a, 2001a) indicated that irrespective of soil type biotite generally occurred as thick particles with different stages of layer separation. They are weathered through layer separations and bending at their edges. At the edges of these particles, layer separation indicated the formation of a vermiculite rim around the particles as a result of replacement of interlayer K of biotite. In contrast, the replacement of interlayer K of muscovite was not substantial as evident from a general lack of interlayer opening. Pal *et al.* (2001a) however observed weak to moderate layer separation at the edge of muscovite in some soils and opined that this is due to alteration prior to pedogenesis. Thus the release of K from fine-grained micas of soils is expected not to be similar because they are far from 'ideal' in structure and composition. Zones in a particle may contain layer minerals in different stages of expansion as demonstrated by Pal *et al.* (2000a, 2001a). Therefore, many of the proposed relationships between K release and micas are based on results obtained from specimen micas and not from soil micas and thus they are speculative (Rich, 1972; Sarma, 1984; Wilson, 1999).

So far attempts made in highlighting the precise nature of soil mica in the silt and clay fractions of Indian soils have been based on the X-ray intensity ratio of peak heights of 001 and 002 basal reflections of mica (Kapoor, 1972). The ratio is greater than unity in the silt and clay fractions of major soils of India (Table 1). However, in soils of Brahmaputra alluvium (BA) and black soils in alluvium of weathering Deccan basalt, this ratio is close to unity particularly in their clay fractions. The ratio >1 may apparently suggests the muscovitic character of mica but in reality it indicates the presence of both muscovite and biotite minerals (Pal *et al*., 2000a). If muscovite minerals were present alone the ratio would have been very close to unity (Tan, 1982). In the event of a mixture of these two micas, both will contribute to the intensity of the 1.0 nm reflections, whereas contribution of biotite to the 0.5 nm reflection would be nil or negligible, thus giving a higher value to the intensity ratio of these reflections (Fig.2) (Kapoor, 1972). According to this criterion, silt fractions of alluvial soils of Indo-Gangetic plains (IGP) and BA, ferruginous and black soils and also the clay fractions of soils of IGP and ferruginous soils contain both muscovite and biotite. But the clay fractions of soils of BA and black soils are more muscovitic in character (Table 1). The enrichment of soils with muscovite is not favourable so far as the K release and available K status are concerned. This is evidenced with the reduced rate of K release from black soils and soils of BA against much higher rate of K release from soils of IGP and ferruginous soils when they were subjected to repeated batch type of Ba-K exchange (Fig.3) (Pal *et al*., 2001a).

A need of a selective quantification of biotite mica in the common situation in soils containing mixtures of biotite and muscovite was planned through an experiment by Pal *et al.*(2006a) wherein the contents of biotite in Vertisols and their size fractions were estimated through a rigorous and exhaustive Ba-K exchange reaction. The cumulative amount of K released at the end of final extraction when release of K almost ceased, was considered as released K mainly from biotite (Fig. 4). The amount of clay, silt and sand biotites in representative Vertisols of central India ranged from 1.0 to 1.6, 0.2 to 0.3 and 0.2 to 0.4 %, respectively. In <2 mm fine earth fraction, biotite quantity does not exceed 1%, which constitutes about 6-8% of total micas. For any size fraction, the cumulative amount of K released on biotite weight

Table 1. *X-ray intensity ratio of the peak heights of 001/002 basal reflection in the silt and clay fractions*[a]

Benchmark Soil/Soil Series	Parent material	Size fractions	
		50-2 mm	<2 mm
Holambi (AS-SA)[c] (Udic Ustochrept)	IGP[b]	2.14	2.63
Hissar (AS-SA) (Typic Ustochrept)	IGP	2.05	2.57
Totpara (AS-SH) (Aeric Fluvaquent)	IGP	2.27	2.73
Kanagarh (AS-SH) (Udic Ustochrept)	IGP	1.48	1.60
Dahotia (AS-PH) (Typic Haplaquept)	BA	1.47	1.10
Akahugaon (AS-PH) (Typic Haplaquept)	BA	1.70	1.04
Aroli (BS-SH) (Typic Chromustert)	DBA	1.80	1.05
Nimone (BS-SA) (Typic Chromustert)	DBA	1.90	1.00
Kasireddipalli (BS-SA) (Typic Pellustert)	DBA	1.56	1.04
Kheri (BS-SH) (Typic Chromustert)	DBA	1.87	1.01
Sarol (BS-SH) (Typic Chromustert)	DBA	1.50	1.04
Patancheru (FS-SA) (Udic Rhodustalf)	GG	1.77	1.80
Nalgonda (FS-SA) (Udic Rhodustalf)	GG	2.00	1.87
Dyavapatna (FS-SA) (Udic Rhodustalf)	GG	2.25	2.16

[b] IGP=Indo-Gangetic alluvium; DBA-Deccan basalt alluvium; GG=Granite-gneiss

[c] AS-SA = Alluvial soil of semi-arid climate; AS-SH = Alluvial soil of sub-humid climate; AS-PH = Alluvial soil of per-humid climate; BS-SH = Black soil of sub-humid climate; BS-SA = Black soil of semi-arid climate; FS-SA = Ferruginous soil of semi-arid climate.

[a] Adapted from Pal *et al*. (2006a).

basis follows: > cumulative amount of K released on whole mica weight basis > cumulative amount of K released on weight basis of size fraction (Table 2). The significant positive correlations between cumulative K release from sand, silt and clay and their corresponding total K contents, respectively (Table 3), indicates

Table 2. *Cumulative K release from a representative Vertisol and its size fractions*

Horizon	Depth (cm)	Fine earth (<2mm) cumulative K release in 75 extractions			Sand (2 - 0.05 mm) cumulative K release in 10 extractions			Silt (0.05 -0.002 mm) cumulative K release in 35 extractions			Clay (<0.002 mm) cumulative K release in 60 extractions		
		SF*	MB	BB	SF	MB	BB	SF	MB	BB	SF	MB	BB
						mg K 100g-1							
Ap	0-15	69	429	6059	20	272	7000	16	191	7004	114	561	6990
Bw1	15-41	41	277	4230	12	162	7006	15	195	7009	92	509	6998
Bw2	41-70	39	267	4097	23	297	6997	13	184	7011	88	502	6999
Bss1	70-95	45	261	4638	15	191	6986	14	161	6990	91	433	7000
Bss2	95-135	49	286	4793	24	334	6991	15	162	6991	92	462	6999
Bss3	135-155	37	235	3849	13	147	6907	16	184	7008	94	471	6984

*SF = on the basis of size fraction; MB = on the basis of mica content; BB = on the basis of biotite content

Adapted from Pal et al. (2006a)

that the K release is a function of total K content in micas and feldspars. However, the positive correlations between total K contents in sand, silt, clay and soil and their mica contents (Table 3) indicate the predominant influence of mica to supply K to the plants grown in Vertisols. Further, significant positive correlations between cumulative K release of sand, silt, clay and soil and their respective mica contents (Table 3) indicate that the K release from either the soils or different size fractions, are controlled mainly by mica. However, better correlations than those between cumulative K release of sand, silt, clay and soil and their biotite contents (Table 3) provide incontrovertible evidence that the K release in soils is primarily controlled by biotite mica. This further supports the earlier observations on the inertness of muscovite mica in releasing K in the presence of biotite (Pal *et al*., 2001a).

Potassium (K) adsorption and low charge vermiculite/high charge smectite

Major soils of India do not adsorb/fix higher amount of K as evident from their low to moderate values of exchangeable potassium percentage (EPP) within 0.5 m of the profile; EPP for majority of the IGP soils ranges from 3 to 8 % (Pal *et al*., 2010), for Vertisols (BS) it ranges from 1 to 2 % (Pal *et al*., 2003a) and for ferruginous soils (FS) it ranges from 3 to 4 % (Murthy *et al*., 1982). It is quite often reported in the literature that micas, hydrous micas and vermiculites have high adsorption/fixation

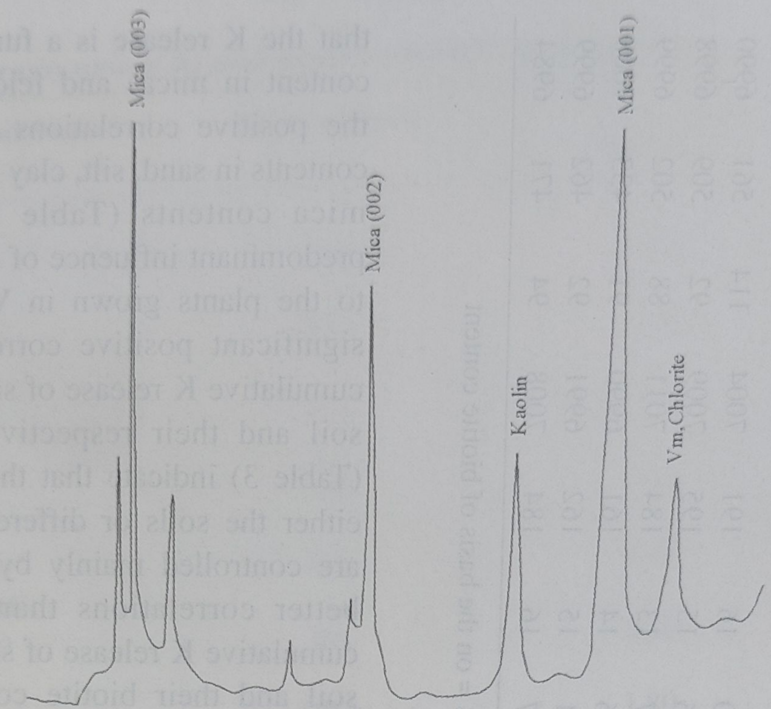


Fig. 2. *XRD diagram showing the basal reflections of the micaceous minerals of soils. The ratio of the 001 and 002 reflections shows much more than a unity.*

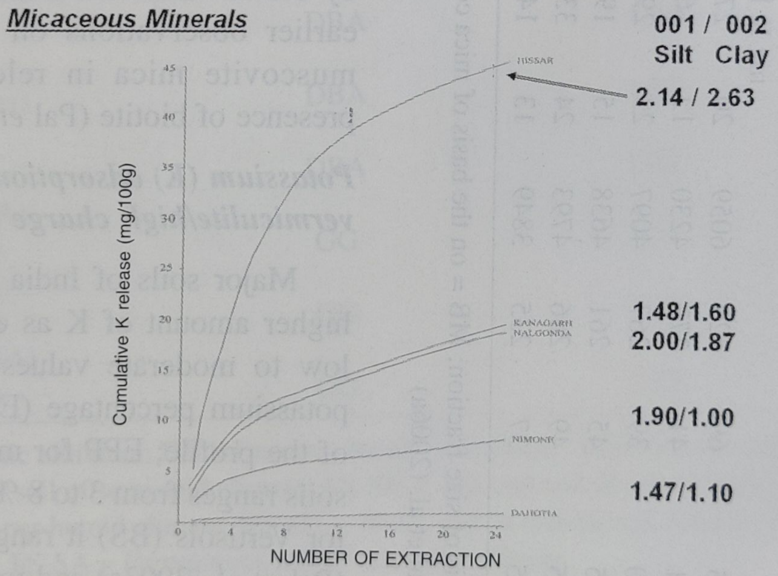


Fig.3. *Relation between cumulative K release of soils and number of extractions: Hissar, representative of IGP soils of SA climate; Kanagarh, representative of IGP soils of SH climate; Dahotia, representative of BA soils of PH climate; Nimone, representative of black soils of SA climate; Nalgonda, representative of ferruginous soils of SA climate. (Please refer to 001/002 ratio of peak heights of mica in table 1).*

Table 3. *Coefficient of correlation among various soil characteristics.*

	Parameter	r
Cumulative K of sand	Total K in sand	0.635**
Cumulative K of silt	Total K in silt	0.771 **
Cumulative K of clay	Total K in clay	0.822**
Total K in sand	Sand mica	0.933**
Total K in silt	Silt mica	0.766**
Total K in clay	Clay mica	0.981**
Total K in soil	Soil mica	0.979**
Cumulative K of sand	Sand mica	0.524*
Cumulative K of silt	Silt mica	0.694**
Cumulative K of clay	Clay mica	0.851**
Cumulative K of soil	Soil mica	0.429*
Cumulative K of sand mica	Sand biotite	0.894**
Cumulative K of silt mica	Silt biotite	0.917**
Cumulative K of clay mica	Clay biotite	0.978**
Cumulative K of soil mica	Soil biotite	0.435*

*Significant at 0.05 level; ** Significant at 0.01 level
Adapted from Pal *et al.* (2006a)

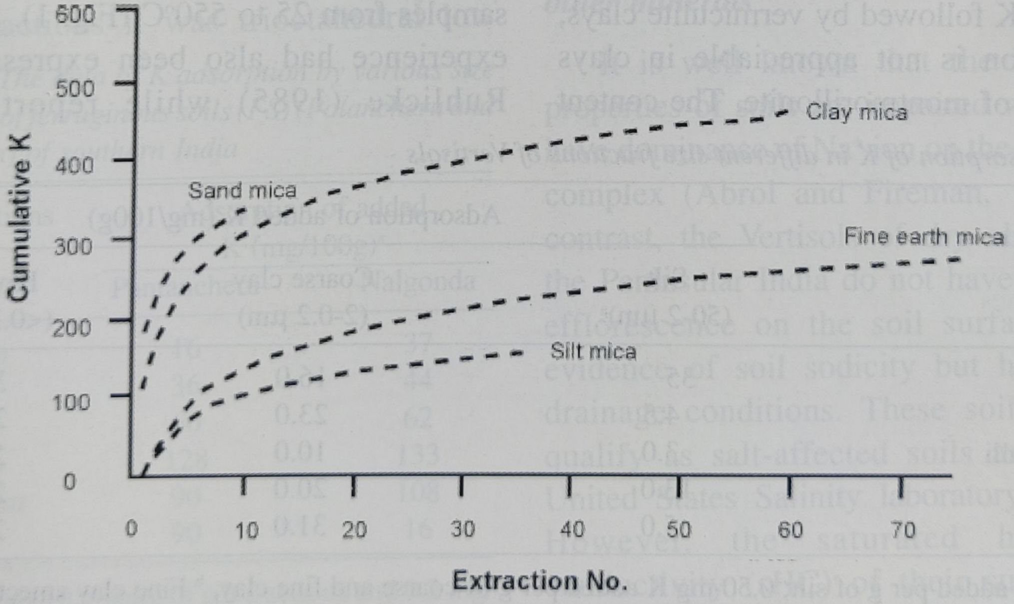


Fig. 4. *Relationship between numbers of extractions and cumulative K release (mg/100 g^{-1} mica) of micas in various size fractions of a Vertisol. Adapted from Pal et al.(2006a).*

properties while smectites and kaolinites have low capacities. However, if mica is understood a mineral that does not expand on being saturated with divalent cations, it is difficult to understand how it can adsorb/ fix added K (Sarma, 1976). In such reactions interlayer charge density of the mineral is of fundamental importance. Kaolinites are of no significance in such a reaction while vermiculites will be converted to mica by layer contraction due to K. Smectites would not possess this property as their layer charge is too low (Brindley, 1966) and they do not adsorb K selectively (Rich, 1968) unless the charge density is high (Pal and Durge, 1989). Schwertmann (1962) indicated that some soil smectites have a greater capacity to fix K than do many of the specimen type smectites. Bajwa (1980) has pointed out that beidellite soil clays are greater fixers for added K followed by vermiculite clays, and fixation is not appreciable in clays consisting of montmorillonite. The content of smectite in BS increases with the decrease in particle size and the fine clay fractions contain its highest amount. Despite this fact fine clay smectites do not participate in adsorption/fixation of added K as evident from their comparable amount of adsorbed K (Table 4). The reason is that the fine clay smectites of benchmark Vertisols of central and western India is nearer to montmorillonite of the montmorillonite-nontronite series (Pal and Deshpande, 1987a) and do not adsorb K selectively because of their low layer charge (Pal and Durge, 1987a). Therefore, the observed low K adsorption in these smectites (Table 4) is due to the presence of vermiculite, which is generally not detected on glycolation of Ca-saturated samples but can be detected by a progressive reinforcement of the 1.0 nm peak of mica while heating the K-saturated samples from 25 to 550°C (Fig. 1). Similar experience had also been expressed by Ruhlicke (1985) while reporting K

Table 4. *Adsorption of K in different size fractions of Vertisols*

Soil Series	Adsorption of added K (mg/100g)		
	Silt (50-2 μm)[a]	Coarse clay (2-0.2 μm)	Fine clay (<0.2 μm) [b]
Aroli	35	16.0	30.0
Sarol	4.5	23.0	25.0
Kasireddipalli	3.0	10.0	25.0
Nimone	13.0	20.0	28.0
Kheri	5.0	31.0	28.0

[a]0.25 mg K added per g of silt; 0.50 mg K added per g of coarse and fine clay,ʼ [b] Fine clay smectites did not adsorb added K in proportion to their high amount indicating their no K-selectivity.

Adapted from Pal and Durge (1987).

adsorption of 60 mg K/100g in bentonite (montmorillonite) deposit. The content of vermiculite was quantified following the method of Alexiades and Jackson (1965) by Pal and Durge (1987) and it ranged from 5 to 9% in the fine clay of Vertisols. Pal and Durge (1987) thus, concluded that the observed K adsorption by the silt and clay fractions is due to the presence of vermiculite and not due to smectite. This indicates that K loss due to adsorption/ fixation in the Vertisols is very less. Similar observation was also made by Pal *et al.* (1993) for K adsorption in FS (Table 5). The fine clay fractions of FS though contained the highest amount of smectite did not participate in K adsorption because the fine clay smectite was mostly low charge dioctahedral smectite. The observed K adsorption in the coarser fractions of FS was attributed to vermiculite and in the finer fractions it was trioctahedral low charge vermiculite/high charge smectite. This smectite could only be detected by their expansion to 1.7 nm on glycolation and by rapid contraction to 1.0 nm on K saturation at 110^{0}C.

Table 5. *The data of K adsorption by various size fractions of ferruginous soils (FS) (Patancheru and Nalgonda) of southern India*

Size fractions	Adsorption of added K (mg/100g)[a]	
	Pantancheru	Nalgonda
50-20 µm	16	37
20-6 µm	36	44
6-2 µm	60	62
2-0.6 µm	128	133
0.6-0.2 µm	90	108
<0.2 µm	90	16

[a] K added was 0.1 mg/g of silt fractions and 0.2 mg/ g of clay fractions

Adapted from Pal *et al.* (1993).

In contrast to the fine clay low charge dioctahedral smectites of Vertisols and FS, trioctahedral smectites of some alluvial soils do adsorb K selectively (Table 6) and rate of K adsorption is almost proportional to the content of smectite which increases with the decrease of particle size (Pal and Durge, 1989). These smectites are easily detected that expand to 1.7nm on glycolation but contract readily to 1.0 nm on K saturation at 110^{o}C indicating their high layer charge density (Pal *et al.*, 1989).

Physical properties of soils and minerals

Hydraulic properties of soils and clay and other minerals

It is well known that the hydraulic properties of soils are impaired when they have dominance of Na^{+} ion on the exchange complex (Abrol and Fireman, 1977). In contrast, the Vertisols of dry climates of the Peninsular India do not have any salt-efflorescence on the soil surface as an evidence of soil sodicity but have poor drainage conditions. These soils do not qualify as salt-affected soils as per the United States Salinity laboratory criteria. However, the saturated hydraulic conductivity (sHC) of their subsoils is adversely affected due to clay dispersion and clogging of pores caused by exchangeable magnesium (Balpande *et al.*, 1996; Vaidya and Pal, 2002). This confirms that saturation of Vertisols with Na^+ and Mg^{+2} ions block small pores in the soil. In other words, Mg^{2+} ions are less efficient than Ca^{2+} ions in flocculating soil colloids (Rengasamy *et al.*, 1986), although the United States Salinity Laboratory (Richards, 1954) grouped Ca^{2+} and Mg^{2+} together as both the ions improve soil structure. The sHC is further impaired even by a low level of exchangeable sodium percentage (ESP) (> 5, < 15) (Balpande *et al.*, 1996) to < 5 mm/hr, causing > 50% reduction in cotton yield (Kadu *et al.*, 2003) because large amounts of smectite minerals (100g of soil may contain 40-50 g of smectite, Pal *et al.*, 2000a) in Vertisols. Thus, the current lower limit of 15 ESP of the United States Salinity Laboratory for all the soils is arbitrary thereby necessitating evaluation of lower limit of ESP. In order to validate this, Pal *et al.* (2006b) undertook an extensive study on Vertisols with and without soil modifiers (Ca-zeolites and gypsum), representing a climosequence from sub-humid moist (SHM) to arid dry (AD) climate and occurring in major states of the Peninsular India. The results of this study indicate that the release of Ca^{2+} ions from soil modifiers prevented the rise in pH and ESP and modified sHC (>10 mm/hr) amidst high ESP, which supports fairly well the performance of rain-fed crops. Therefore, fixing a lower limit of sodicity at ESP > 40 for soils of the IGP (Abrol and Fireman 1977), at ESP > 5 but < 15 for Indian Vertisols (Kadu *et al.*, 2003), at ESP 6 for Australian soils or at ESP > 15 for all soil types (Soil Survey Staff, 1999) is incompatible with fairly well performance of crops in highly sodic Vertisols with soil modifiers especially of Ca-zeolites (Fig.5) (Pal *et al.*, 2006b). The impairment of sHC of soils mediated by dispersibility is the most important factor for soil degradation (Sumner, 1995), and thus, the characterization of sodic soils on the basis of sHC appears to be most appropriate parameter where 50% reduction in crop

Table 6. *Asorption of K in different size fractions of alluvial IGP and BV*

Size fractions	Adsorption of added K (mg/100g)[a]		
	Holambi (IGP)	Kanagarh (IGP)	Dahotia (BV)
20-6 μm	6.6	9.7	0.5[b]
6-2 μm	11.8	19.1	1.0
2-0.6 μm	30.4	52.9	26.4
0.6-0.2 μm	45.5	63.7	31.0
<0.2 μm	67.7	79.3	50.0

[a] K added 1 mg per g of silt and 2 mg per g of clay fractions· [b] Showing high K selectivity of smectite.

Adapted from Pal and Durge (1989).

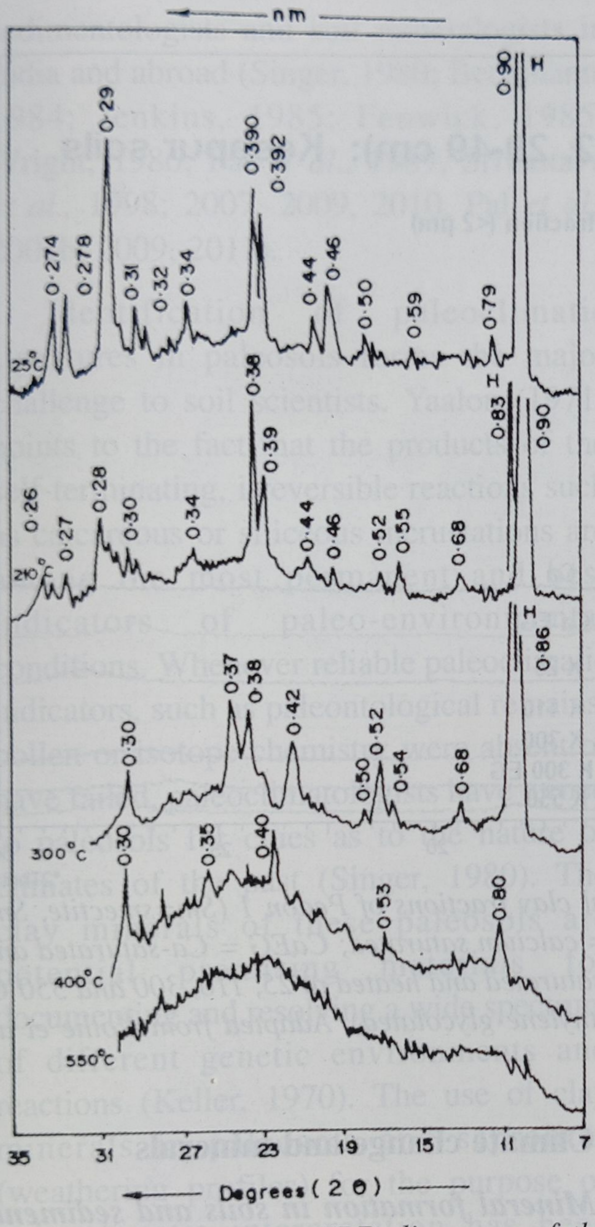


Fig. 5. *Representative XRD diagrams of the powdered sand fractions of shrink-swells in semi-arid part of the Western Ghats: H=heulandites (Ca-zeolites). Adapted from Bhattacharyya et al. (1999).*

yields has been recorded. Therefore, Pal *et al.* (2006b) advocated a value of sHC < 10 mm h^{-1} (as weighted mean in 1m depth of soil) instead of ESP or SAR as the important crop limiting soil factor. Therefore, the identification of Ca-zeolites and gypsum is very necessary. They can be easily detected by thin section studies and /or XRD technique. However, their presence can be readily realised when the summation of extractable bases are in excess of the CEC of soils (Bhattacharyya *et al.*, 1993; Pal *et al.*, 2003a, 2006b, 2011) due to release of extra Ca ions from soil modifiers by the exchanger solution during the extraction of exchangeable cations of soils.

Dispersibility of clay colloids impairing the sHC of soils is caused by ESP or to some extent exchangeable magnesium percentage (EMP) in the presence or absence of soil modifiers. However, the sHC of zeolitic Vertisols of Marathwada region in Maharashtra state of the semi-arid part of western India indicated a value <10 mm/hr, though they are non-sodic soils (Typic Haplusterts) (Zade, 2007). Such Vertisols have neutral to mildly alkaline pH, ESP < 5, but have increasing trend in EMP with depth, and in some pedons EMP is more than ECP (exchangeable calcium percentage) beyond 50 cm depth. Mineralogical studies indicate the presence of palygorskite mainly in the silt and coarse clay fractions (Fig. 6) (Zade, 2007; Kohle *et al.*, 2012). This mineral is the most magnesium rich among the common clay minerals (Weaver and Pollard, 1973; Singer, 2002). Therefore, Vertisols with palygorskite mineral are rich in EMP, which causes enormous dispersion of clay colloids

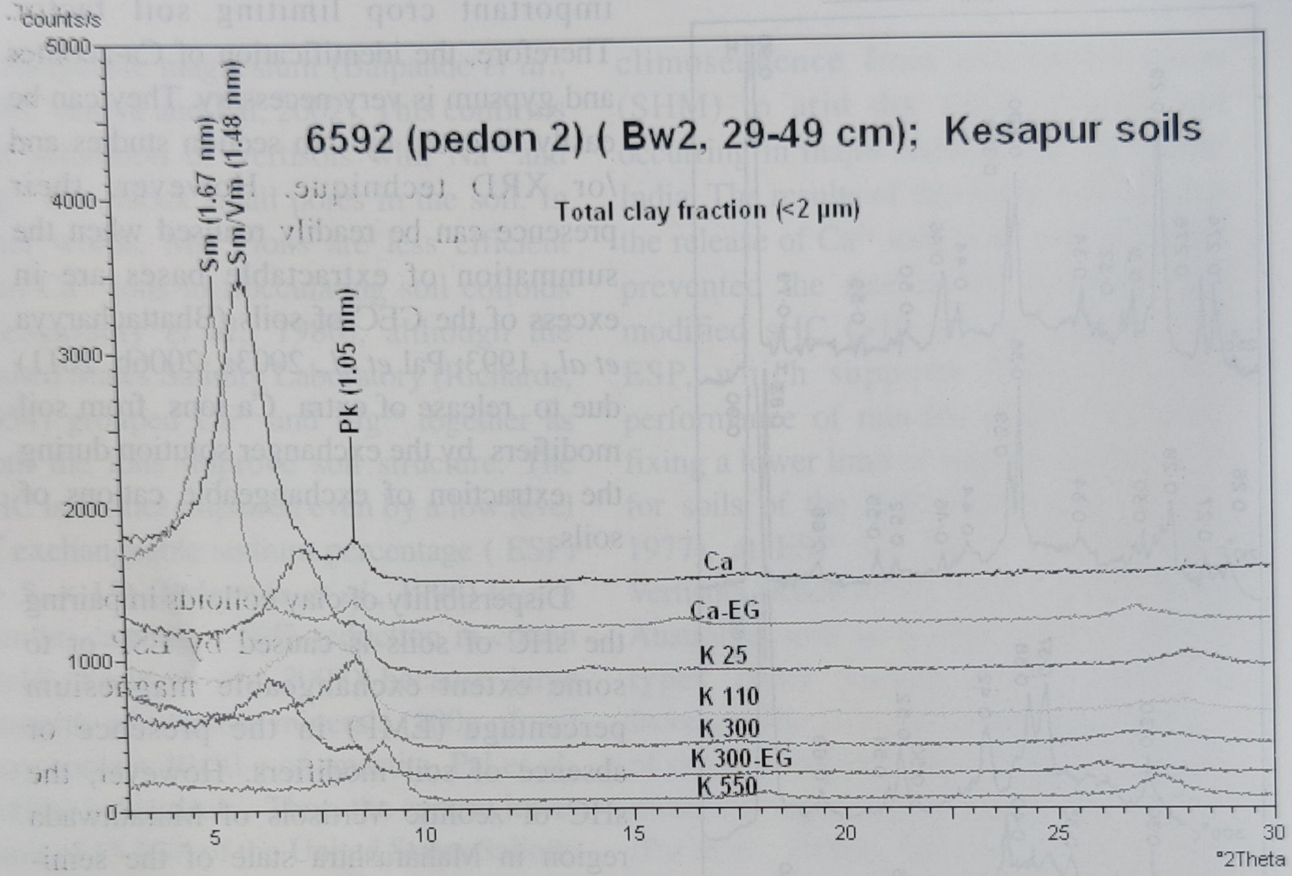


Fig. 6. *Representative X-ray diffractograms of total clay fractions of Pedon 1 (Sm=smectite, Sm/Vm=smectite or vermiculite, Pk=palygorskite, Ca = calcium saturated; CaEG = Ca-saturated and ethylene glycolated; K25°/K110°/K300°/K550° = K saturated and heated at 25, 110, 300 and 550°C. K300°EG= K saturated and heated at 300° and ethylene glycolated). Adapted from Kolhe et al. (2011).*

that form a 3D mesh in the soil matrix. This causes drainage problem when such soils are irrigated, a predicament for crop production. In view of their poor drainage conditions and loss of productivity, non-sodic Vertisols (Typic Haplusterts) with palygorskite minerals needs to be considered as naturally degraded soils. Similar soils may be occurring elsewhere in the world and thus, a new initiative to classify them is warranted.

Climate change and minerals

Mineral formation in soils and sediments as signatures of climate change

Paleopedological research unravels the signatures of climate change that generally remain stored in soils and sediments of the past (Pal *et al.*, 2000a) and such soils are known as paleosols, formed on a landscape of the past (Valentine and Dalrymple, 1976). Studies on paleosols have caught the attention of the pedologists, sedimentologists and soil mineralogists in India and abroad (Singer, 1980; Beckmann, 1984; Jenkins, 1985; Fenwick, 1985; Wright, 1986; Pal *et al.*, 1989, Srivastava *et al.,* 1998; 2007, 2009, 2010, Pal *et al.*, 2001b, 2009, 2011).

Identification of paleoclimatic signatures in paleosols forms the major challenge to soil scientists. Yaalon (1971) points to the fact that the products of the self-terminating, irreversible reactions such as calcareous or siliceous incrustations are among the most permanent and best indicators of paleo-environmental conditions. Whenever reliable paleoclimatic indicators, such as paleontological remains, pollen or isotope chemistry were absent or have failed, paleoclimatologists have turned to paleosols for clues as to the nature of climates of the past (Singer, 1980). The clay minerals of these paleosols are potential promising materials for documenting and resolving a wide spectrum of different genetic environments and reactions (Keller, 1970). The use of clay minerals in paleosols and saprolites (weathering profiles) for the purpose of paleoclimatic interpretation has been explained in detail by Singer (1980). It is often difficult to determine as to which minerals are diagnostic of different climatic zones. However, those clay minerals which occur most frequently can be considered to have climatic significance (Tardy *et al.,* 1973). For example, minerals such as kaolinite often remain unaltered through subsequent changes in climate, and therefore, may preserve a paleoclimatic record. Singer (1980) indicated that other layered silicates at a less advanced stage of weathering may adjust to subsequent environmental changes and thus may lose their interpretative value for paleoclimatic signatures. However, several Indian researchers have considered minerals of intermediate weathering stage as potential indicators of paleoclimatic changes in parts of central India and Gangetic Plains (Pal *et al.*, 1989; Srivastava *et al.,* 1998; Pal *et al.*, 2009, 2011). They have demonstrated how secondary minerals like di- and trioctahedral smectites (DSm and TSm), smectite-kaolin interstratified minerals (Sm/K), hydroxy-interlayered smectite (HIS), hydroxy-interlayered vermiculite (HIV), pseudo-chlorite (PCh) of intermediate weathering stage, and $CaCO_3$ of pedogenic (PC) and non-pedogenic (NPC) origin can be regarded as potential indicators of paleoclimatic changes in major soil types of India and also in paleosols of the alluvial sediments of the Himalayan river systems and Cratonic source from Peninsular India.

Di- and trioctahedral smectite as evidence for paleoclimatic changes

Well crystallized dioctahedral smectites as the first weathering product of Peninsular Gneiss partly transformed to kaolin in ferruginous soils (Alfisols) formed in a pre-Pliocene tropical humid climate (Pal *et al.*, 1989). Such kaolin (Kl) is not a discrete kaolinite as XRD diagrams of its Ca-saturated and glycolated sample indicates the broad base of 0.72 nm peak and tails towards the low angle. On heating the K-saturated sample at 550°C, the 0.72 nm peak disappears, confirming the presence of kaolin and simultaneously reinforces the 1.0 nm region at much higher degree even in presence of 1.4 nm minerals, indicating the presence of KI-HIV/HIS (kaolin interstratified with either hydroxy-interlayered vermiculite, HIV or smectite, HIS) (Fig. 7). Later with the termination of humid climate, both these clay minerals were preserved to the present. Therefore, the ferruginous Alfisols overlying the saprolites dominated either by dioctahedral smectite or kaolin are relict paleosols (Pal *et al.*, 1989; Chandran *et al.*, 2000), which have been affected by the climatic change from humid to drier conditions during the Plio-Pleistocene transition period. It is evidenced by the formation of trioctahedral smectite in the present dry climate from the sand and silt size biotite (Fig.8a), which survived weathering during the earlier humid climate. This smectite is high charge smectite or low charge vermiculite that expands to 1.7 nm on glycolation of Ca-saturated sample but contracts readily to 1.0 nm on K-saturation and heating to 110° C. The present day warm semi-aridic

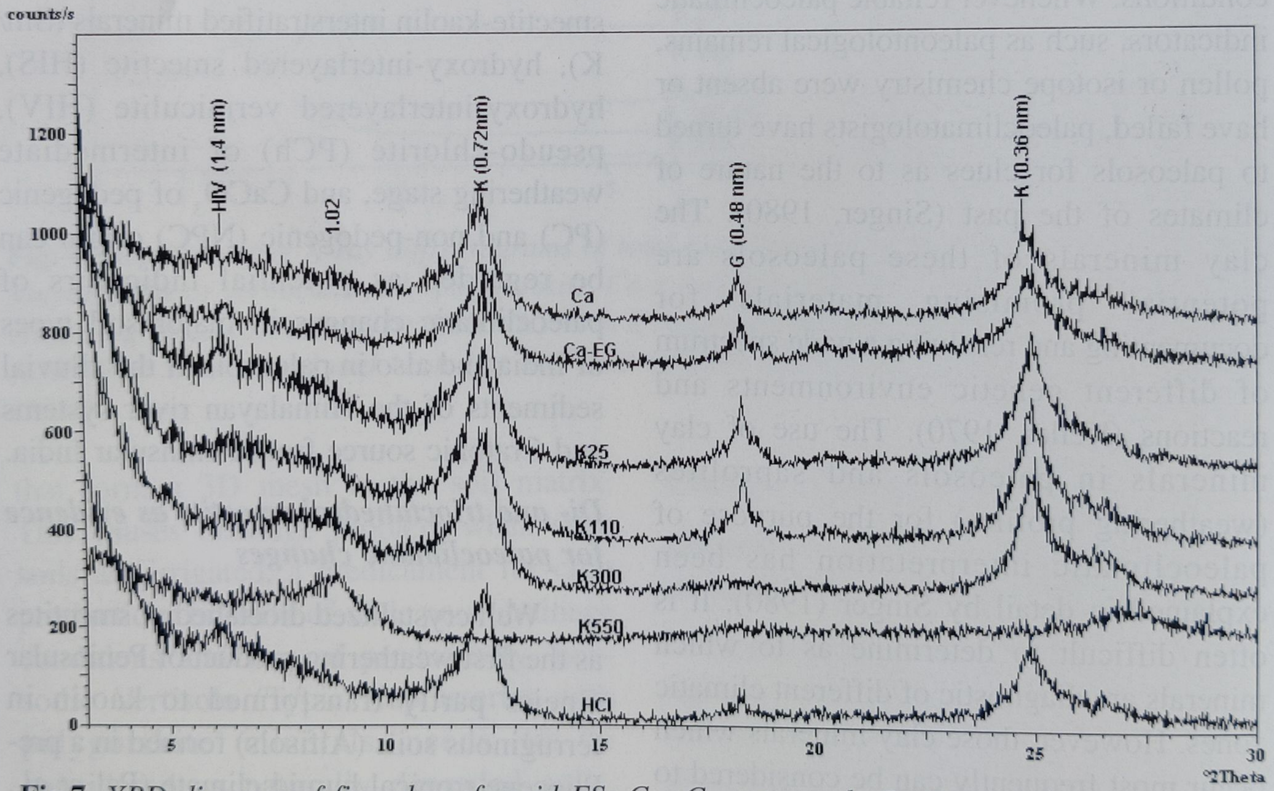
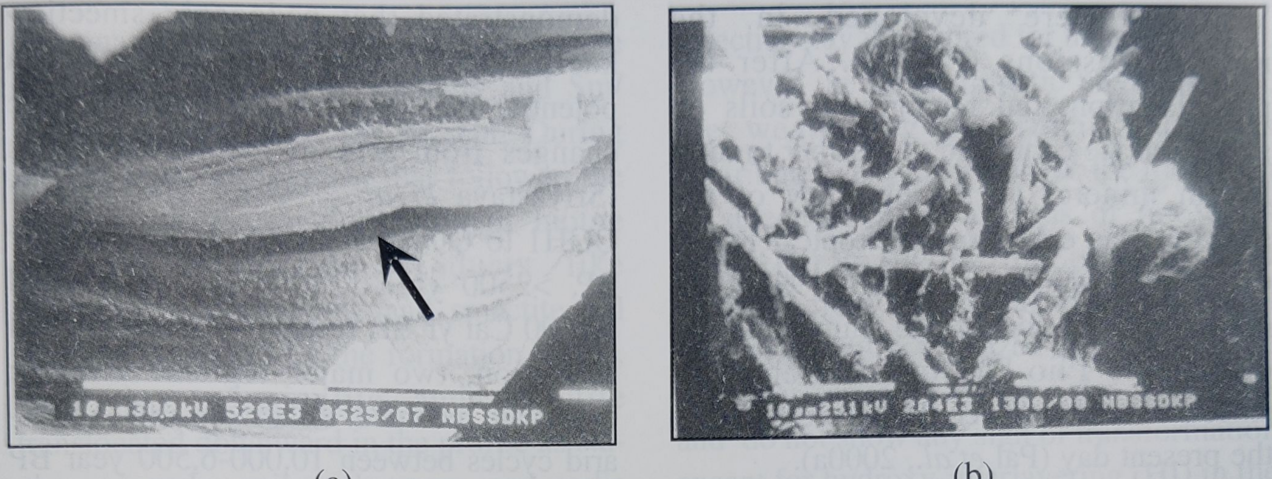


Fig.7. *XRD diagram of fine clay of acid FS: Ca, Ca-saturated; Ca-EG, calcium-saturated and ethylene glycolated-solvated; K25,K110,K300,K550, K-saturated and heated to 25°,110°,300° and 550° C, respectively; HCl, treated with 6N HCl for 30 min at 90° C. HIV, hydroxy-interlayered vermiculite; K, kaolin; G, gibbsite. Adapted from* Chandran *et al.* (2005).



(a) (b)

Fig. 8. *Representative SEM photograph of the formation of vermiculite around biotite particles of ferruginous soils (Alfisols) (a), of PC (lubinites) in ferruginous soils (Alfisols) of semi-arid southern India (b). Adapted from Pal et al. (2000a).*

climatic conditions also favoured the formation of pedogenic calcium carbonate (PC)(Fig.8b) by inducing the precipitation of $CaCO_3$ with a concomitant development of subsoil sodicity (Pal *et al.*, 2000b; 2011). These relict paleosol qualify to be polygenetic soils with strong paleoclimatic potential (Pal *et al.*, 1989).

Red and black soils in semi-arid climatic environments

Occurrence of spatially associated red ferruginous (Alfisols) and black (Vertisols) soils on gneiss under similar topographical conditions are very common in semi-arid region of southern Peninsular India (Pal and Deshpande 1987b). Ferruginous soil clays consist chiefly of kaolin and smectite whereas black soil clays are dominated by low charge dioctahedral smectite. The inverse relation between kaolin and smectite with pedon depth of ferruginous soil clays (Pal *et al.*, 1989) indicated the transformation of smectite to kaolin even though prevailing semi-arid climate can not favour the formation of kaolin at the expense of smectite in slightly acid to moderately alkaline reaction. Similarly, the arid climate cannot yield the huge amount of smectite required for the formation of Vertisols. Earlier studies in southern Peninsular India (Murali *et al.*, 1978; Rengasamy *et al.*, 1978) suggested that kaolinite was formed in an earlier geological period with more rainfall and great fluctuations in temperature, as evidenced by the presence of granitic tors all around such area (Pal and Deshpande 1987b). Therefore, the smectite of Vertisols formed in the earlier humid climate. This was detached from the weathering gneissic rock and transported downstream and deposited in low-lying areas following the landscape reduction process and the typical

Vertisols were developed in the microdepressions (Fig. 9). After the peneplanation, red ferruginous soils on stable surface continued to weather to form kaolin mineral as the stability of the smectite was ephemeral in tropical humid climate (Bhattacharyya *et al.*, 1993). But due to termination of the humid climate during the Plio-Pleistocene transition, smectite and kaolin could be preserved to the present day (Pal *et al.*, 2000a).

Clay minerals in soils of the Indo-Gangetic Plains (IGP)

Transformation of clay minerals in a soil chrono-association comprising 5 fluvial surfaces (QGH1 to QGH5) of the IGP between Ramganga and Rapti rivers, demonstrated that pedogenic smectite-kaolin (Sm/K) can be considered as a potential indicator for Holocene climatic changes from arid to humid conditions (Srivastava *et al.*, 1998). The ages of QGH1 to QGH5 are <500 yr BP, >500 yr BP, >2500 yr BP, 8000 Cal yr BP and 13,500 Cal yr BP, respectively. During soil formation, two major regional climatic cycles are recorded. Relatively arid to semi-arid cycles between 10,000-6,500 year BP and 4,000 year BP till present was punctuated by a warm and humid climate. Biotite weathered to trioctahedral vermiculite and smectite in the soils during arid conditions that was unstable and transformed to Sm/K during the following warm and humid climate phase (7400-4150

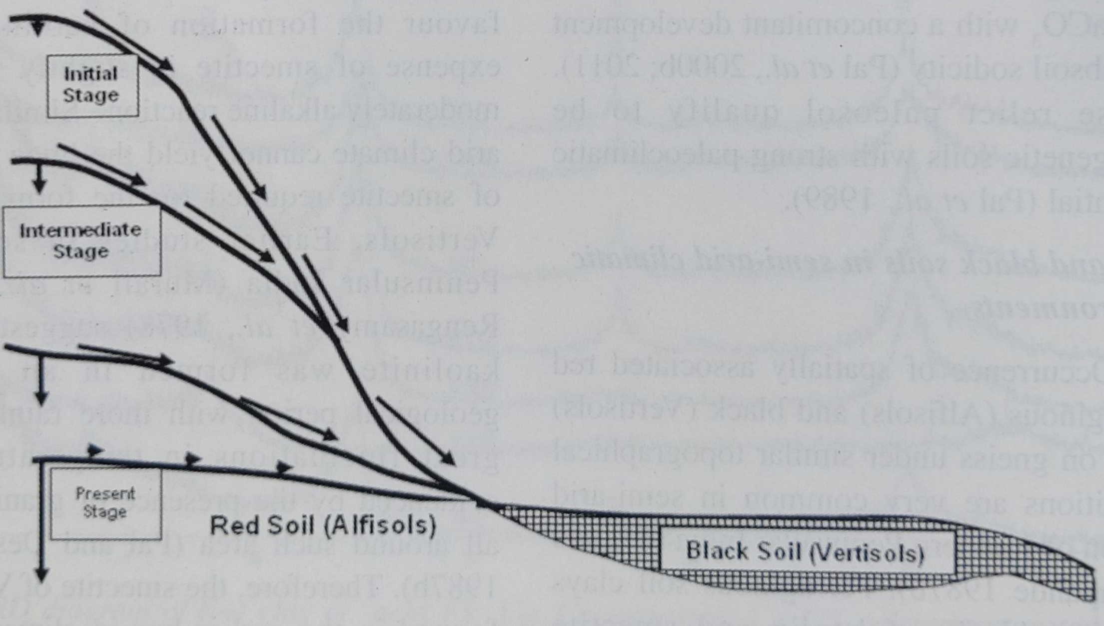


Fig. 9. Schematic diagram of the pedon site of red soils (Alfisols) and black soils, (Vertisols) showing the landscape reduction process explaining the formation of spatially associated red and black soils. Adapted from Pal (2008).

Cal year BP). When the humid climate terminated, vermiculite, smectite and Sm/K were preserved to the present. During the hot semi-arid climate that followed the humid climate, transformation of biotite into its weathering products like trioctahedral vermiculite and smectite did continue. Initiated by the formation of PC, fine clay vermiculite and smectite translocated downward in the profile as Na-clay, to make soils calcareous and sodic (Pal *et al.*, 1994, 2003b). This pedogenetic process with time become an example of self -terminating process (Yaalon, 1971) exhibiting their polygenetic features.

Vertisols, carbonate minerals and climate change

Smectitic Vertisols occur in humid tropical (HT), sub-humid moist (SHM), sub-humid dry (SHD), semi-arid moist (SAM), semi-arid dry (SAD) and arid dry (AD) climatic environments in Deccan basalt area (Pal *et al.*, 2009). It is well known that smectites are ephemeral in HT climate as they readily transform to kaolin (Pal *et al.*, 1989; Bhattacharyya *et al.*, 1993). The formation of Vertisols in HT climate has been possible because smectite of Sm/K and Ca-zeolites created conducive chemical environment necessary for the formation and persistence of Vertisols in lower topographic situation (Bhattacharyya *et al.*, 1993, 1999). It is equally difficult to understand the formation of Vertisols in SHM, SHD, SAM, SAD and AD climates, since a large amount of smectite clay is required for their formation. However, in these climatic environments, the weathering of primary minerals contributes very little towards the formation of smectites. XRD analysis of fine clays (Fig. 10) indicates that smectites of Vertisols from sub-humid to arid climates are fairly well crystallized as evident from a regular series of higher order reflections and do not show any sign of transformation except for hydroxy-interlayering (HI) in the smectite interlayers (Pal *et al.*, 2000a; Srivastava *et al.*, 2002). Such interlayering

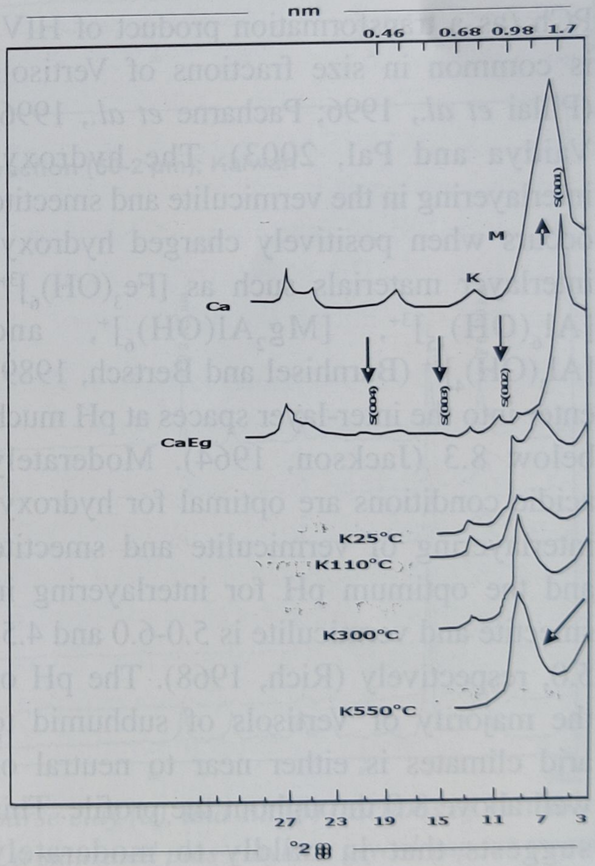


Fig. 10. *Representative X-ray diffractograms of fairly well crystalline fine clay smectite of Vertisols despite having partial hydroxy-interlayering. Adapted from Pal (2003).*

was also noticed in vermiculite of the silt and coarse clay fractions (Fig. 11) that resulted finally in the formation of pseudo-chlorite (PCh). HI in smectite interlayers is identified from the broadening of the low angle side of the collapsed 1.0 nm peak of K-saturated smectite heated to 550°C (Fig. 10). PCh is not a true chlorite as it shows a broad peak around 1.4 nm when K-saturated sample is heated to 550°C (Fig. 11). Thus the presence of hydroxy-interlayered dioctahedral smectite (HIS), hydroxy-interlayered vermiculite (HIV as an alteration product of biotite mica) and PCh (as a transformation product of HIV) is common in size fractions of Vertisols (Pillai *et al.,* 1996; Pacharne *et al*., 1996; Vaidya and Pal, 2003). The hydroxy-interlayering in the vermiculite and smectite occurs when positively charged hydroxy-interlayer materials such as $[Fe_3(OH)_6]^{3+}$, $[Al_6(OH)_{15}]^{3+}$, $[Mg_2Al(OH)_6]^{+}$, and $[Al_3(OH)_4]^{5+}$ (Barnhisel and Bertsch, 1989) enter into the inter-layer spaces at pH much below 8.3 (Jackson, 1964). Moderately acidic conditions are optimal for hydroxyl interlayering of vermiculite and smectite and the optimum pH for interlayering in smectite and vermiculite is 5.0-6.0 and 4.5-5.0, respectively (Rich, 1968). The pH of the majority of Vertisols of subhumid to arid climates is either near to neutral or well above 8.0 throughout the profile. This suggests that in mildly to moderately alkaline conditions of soils, 2:1 layer silicates suffer congruent dissolution (Pal, 1985). Thus, it discounts the hydroxy-interlayering of smectites and vermiculites during the post depositional period of the basaltic alluvium (Pal *et al.,* 2011), likewise the subsequent transformation of vermiculite to PCh. Therefore, the formation of HIS, HIV and PCh does not represent contemporary pedogenesis of Vertisols in the prevailing dry climatic conditions (Pal *et al*., 2011). Vertisols of subhumid to arid climates have both NPC (relict Fe-Mn coated carbonate nodules) and PC (pedogenic $CaCO_3$) (Pal *et al*., 2000b, 2009). Based on ^{14}C dates of carbonate nodules, Mermut and Dasog (1986) concluded that Vertisols with Fe-Mn coated $CaCO_3$ are older soils than those with PCs that are formed in soils of dry climate (Pal *et al*., 2000b). Thus, NPCs were formed in a climate much wetter than the present, which ensured adequate soil water for reduction and oxidation of iron and manganese to form Fe-Mn coatings. The first weathering product of plagioclase-rich Deccan basalt is a low charge di-octahedral smectite (DSm) in aridic to humid climates (Pal and Deshpande, 1987b). Thus, the large amount of DSm formed in an earlier humid climate in the source area as an alteration product of plagioclase in tropical humid climates (Pal *et al*., 1989; Srivastava *et al.,* 1998) and during this weathering vermiculite transformed to HIV, which may have transformed to PCh because HI in vermiculite would occur in acidic soil conditions. However, the formation of HIS in humid tropical climate did not continue as evidenced from the presence of very small

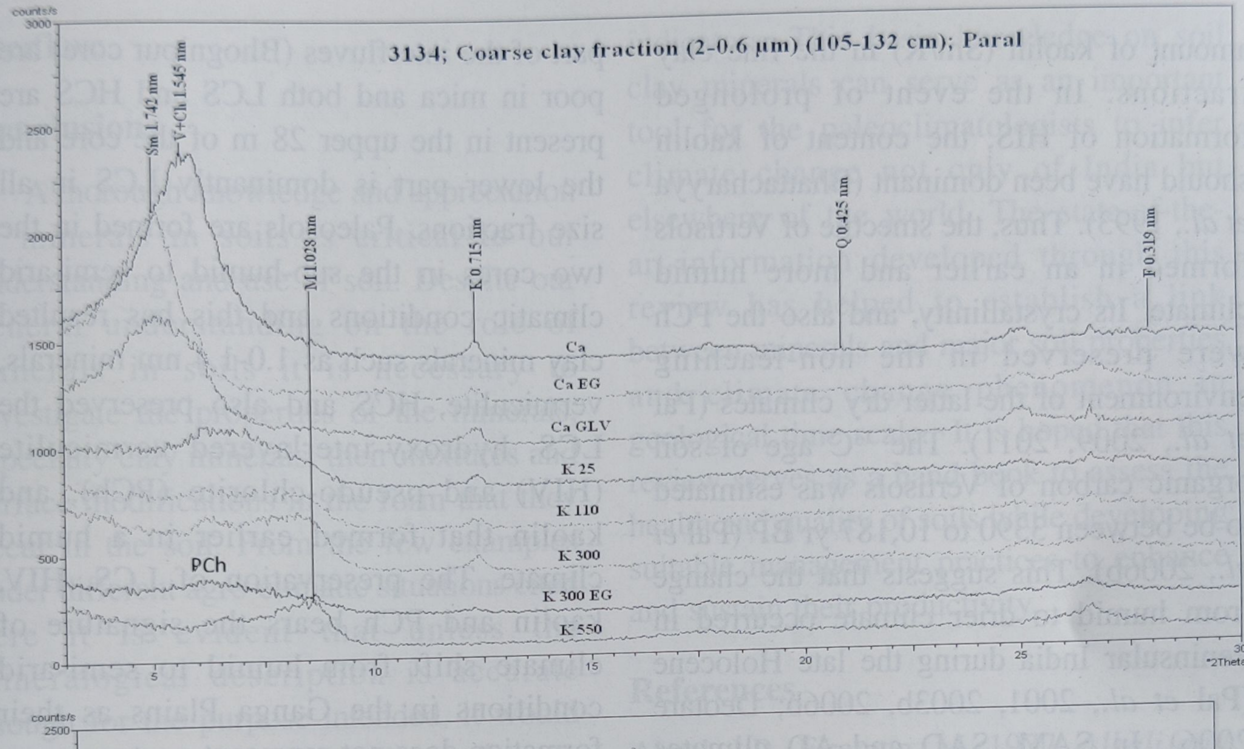


Fig. 11. *Representative X-ray diffractograms of coarse clay (a), and silt (b) fractions of Vertisols of Peninsular India; Ca = Ca saturated; Ca-EG = Ca saturated plus ethylene glycol vapour treated; K25/110/300/550^{0}C=K-saturated and heated to 25^{o}, 110^{o}, 300^{o}, 550°C; 6NHCl = 6N HCl treated silt fraction; Sm = Smectite, V + Ch = vermiculite plus chlorite; PCh= Pseudo chlorite; K = Kaolin; F = Feldspars; Q = Quartz. Adapted from Pal et al.(2003a) and Bhople (2010).*

amount of kaolin (Sm/K) in the fine clay fractions. In the event of prolonged formation of HIS, the content of kaolin should have been dominant (Bhattacharyya *et al*., 1993). Thus, the smectite of Vertisols formed in an earlier and more humid climate. Its crystallinity, and also the PCh were preserved in the non-leaching environment of the latter dry climates (Pal *et al*., 2009, 2011). The ^{14}C age of soil organic carbon of Vertisols was estimated to be between 3390 to 10,187 yr BP (Pal *et al*., 2006b). This suggests that the change from humid to drier climate occurred in Peninsular India during the late Holocene (Pal *et al*., 2001, 2003b, 2006b; Deotare 2006). In SAM, SAD and AD climates Vertisols became more calcareous and sodic (Pal *et al*., 2006b) than those of SHM and SHD climates. Therefore, they qualify to be polygenetic (Pal *et al*., 2001).

Clay minerals record from drill cores of the Ganga Plains

Climate change over the last 100 ka has been manifested in clay mineralogy of paleosols and sediments from two cores (~50 m deep) in the Ganga–Yamuna interfluve in the Himalayan Foreland Basin, India (Pal *et al*., 2011). Core sediments from the northern part of the interfluve (IITK core) are micaceous and dominated by hydroxy-interlayered dioctahedral low-charge smectite (LCS) in fine clay fraction but by trioctahedral high-charge smectite (HCS) in silt and coarse clay fractions. In contrast, core sediments from the southern part of the interfluves (Bhognipur core) are poor in mica and both LCS and HCS are present in the upper 28 m of the core and the lower part is dominantly LCS in all size fractions. Paleosols are formed in the two cores in the sub-humid to semi-arid climatic conditions and this has resulted clay minerals such as 1.0-1.4 nm minerals, vermiculite, HCS and also preserved the LCS, hydroxy-interlayered vermiculite (HIV) and pseudo-chlorite (PCh), and kaolin that formed earlier in a humid climate. The preservation of LCS, HIV, kaolin and PCh bears the signature of climate shift from humid to semi-arid conditions in the Ganga Plains as their formation does not represent contemporary pedogenesis in the present alkaline chemical environment induced by the semi-arid climate. The abundance of LCS sediments in both the cores suggests the role of plagioclase weathering in the formation of LCS. The climatic records inferred from the typical clay mineral assemblages of the two interfluve cores are consistent with the Marine Isotope Stages (MIS) over the last 100 ka. Typical clay mineral assemblage in humid interglacial stages (e.g. MIS 5, 3 and 1) is marked by HIV, LCS and PCh formed under acidic soil conditions. In a drier climate (MIS 4 and 2), formation of trioctahedral HCS from biotite weathering and precipitation of pedogenic $CaCO_3$ were the dominant processes that created conducive environment for illuviation of clays forming argillic (Bt) horizon in the paleosols of the interfluve.

Conclusions

A thorough knowledge and appreciation of minerals in soils is critical to our understanding and use of soil. Despite our general understanding on the role of minerals in soils it is necessary to investigate the properties of the minerals, especially clay minerals, their mixtures and surface modifications in the form that they occur in the soil. From the few examples under different agro-climatic situations cited here it is evident that unless the mineralogical description is accurate enough for the purpose intended, it would not be prudent to look for their significance in soils. With the use of high resolution micro-morphology, mineralogy, and age control data alongside their geomorphologic and climatic history, we can identify and explain many enigmatic situations in soils. Therefore, the future research endeavours should provide adequate knowledge that would explain discretely many of the pedo-edaphological aspects and also the impacts of climate change in soils in terms of minerals in general and clay minerals in particular and their significance for soil as a sustainable medium for plant growth. The mineralogical research work undertaken over the last several decades on important soil/paleosol types and the sediments demonstrates that the pedogenic clay minerals of intermediate weathering stages like HIS, Sm/K, HIV, PCh and pedogenic carbonates can be very useful paleoclimatic indicators. This basic knowledge on soil clay minerals can serve as an important tool for the paleoclimatologists to infer climate change not only of India but elsewhere of the world. The state-of-the-art-information developed through this review has helped to establish a link between minerals and major soil properties and climate change phenomenon in geological time scale. It is hoped that this review serves as a hand book to assess the health and quality of soils while developing suitable management practices to enhance and sustain their productivity.

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