NATURALLY- OCCURRING CLAY -ORGANIC COMPLEX IN INDIAN SOILS

TAPAS BHATTACHARYYA

AUTHOR'S NOTE

I recall someone telling me during the 1990s that, remember how your Ph. D. thesis almost took your life. I don't know about others, but for me, it was tough. Because I took a project for which the required facilities were almost non-existent in my laboratory. I collected permission to work at night in nearly all the laboratories. I did it only through my good behaviour.

I worked up to 16 to 17 hours daily in NRL, IARI. I tried to do justice with my project. There were many hurdles, finances, and mental stress, but I could do that. I was remembering all those well-wishers who came forward to assist me.

I did not find many references on naturally-occurring clay organic complexes in soils; such are still scarce.

This book is meant only for young researchers. Remember I worked with all the old facilities.

I couldn't pursue this line of research. Someone will do.

God bless you all, always.

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NATURE AND CHARACTERISTICS OF CLAYS AND CLAY-ORGANIC COMPLEXES IN MAJOR SOIL GROUPS OF INDIA

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"The union of mineral and organic matter to form the organo-mineral complex (is) a synthesis as vital to the continuance of life as, and less understood than, photosynthesis".

Jacks, 1963

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New Dehi

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1. Introduction

So far, soil studies have always attempted to separate the different fractions, namely, organic matter, amorphous materials and inner-core materials, i.e. crystalline components and then study the various properties of those fractions. Mattson (1930, 1932) concluded that the colloid complex is made up of a relatively inert framework of silica, iron and aluminous materials encased in an active amorphous envelope of a varying compound of silica, alumina and iron with alkalis and alkaline earths (Grim, 1968). It has been found that clay minerals in soil rarely exist as a free entity due to the small particle size and inherent charge characteristics, and they are coated with extraneous materials in most cases. Most soil properties are dependent on the surface reactivity of soil colloids. They are, therefore, likely to be governed not only by the crystalline clay minerals but also by the outer coatings of amorphous inorganic and organic material. Recognition of this fact demands that clay-humus complex be fully characterised for a better understanding of their role in determining various soil properties.

In a review (Jacks, 1963), it was stated that "the union of mineral and organic matter to form the organo-mineral complex (is) a synthesis as vital to the continuance of life as, and less understood than, photosynthesis". Part of the reason it is less understood than photosynthesis is that its importance has not been widely recognised. There are other reasons. The interaction between clays and organic materials in soils is difficult to investigate. Not only are there many uncertainties remaining regarding the constitution of the bulk of the organic material, but the precise condition of the surfaces with which union takes place is seldom known.

These surfaces may be relatively simple, as indicated by the known structures of clay minerals. Still, they may also be surfaces of amorphous or poorly crystallized oxides or hydroxides of silicon, aluminium, and iron, which may present as such or as encrustations on the surfaces of clay minerals. Even for clay minerals with "clean" surfaces, much remains to be learned about the distribution of charges at the surface. Finally, the interaction between inorganic and organic materials occurs in a multi-component system, further complicating the phenomenon. There have been advances in understanding the adsorption of simple and polymeric organic compounds and in the knowledge of the chemical composition and physicochemical properties of the organic in soils, illuminating the interaction mechanism. These advances enable a better appreciation of the rather diverse information concerning the interactions of clays and organic compounds in soils and the properties of the clay-organic complex to be obtained (Greenland, 1965a).

Studies of soils in this particular line were carried out earlier, mostly by Russian authors. However, with the advent of the modern concept of clay minerals, there was more emphasis on relating soil properties to clay mineralogy. Consequently, studies in this direction suffered a setback. The nature of clay-organic complexes has long been a research subject. As far as soils and sediments are concerned, this work has been handicapped by incomplete knowledge of the composition of the organic matter itself, knowledge that is essential for a real understanding of those complexes. Two different approaches have been used to study clay-organic complexes. On the one hand, various extracts and derivatives of organic matter were allowed to react with clays, and the properties of the resulting complex were studied. The other approach has been to utilize organic compounds of known constitution and to deduce the nature of their interaction with clays from their known properties. The latter direction has resulted in considerable fundamental knowledge about the binding mechanisms between various functional groups of organic molecules and clay mineral surfaces. Logic would suggest a similar reactivity for these functional groups where they exist in soil organic matter interaction with clay (Mortland, 1970).

Of the large number and variety of organic compounds, both simple and polymeric, which are known to form complexes with clay minerals (Greenland, 1965a, b; Theng, 1972a), humic substances were among the first to have described as capable of acting in this capacity. Thus, as early as 1874, Schlesinger observed that clays tended to unite with soil humates (Russel, 1973). It was not until the nineteen-thirties, however, that the existence of clay-humic complexes in the soil became widely recognised, their occurrence being responsible for maintaining soil structure and fertility (Allison, 1973). It seems, therefore, ironic that the most important and ubiquitous clay-organic complexes in nature are the least well characterised, a condition ascribed to imperfect knowledge of the chemical constitution of humic substances. Related to this problem is the difficulty or well-nigh practical impossibility of obtaining discretely homogeneous fractions, that is, materials consisting of homopolymeric species different only in terms of molecular weight. Dubach and Mehta (1963) went so far as to state that ".....perhaps no two molecules of humic substances are exactly alike".

Clay minerals can adsorb humic and fulvic acids through association with polyvalent metals at the clay surface. When iron and aluminium hydroxides are polymerized at clay surfaces, an opportunity arises for strong bonding between clay and organic materials to develop. This may involve "ligand exchange" reactions and simple anion exchange. Secondary, non-coulombic interactions can also occur, particularly if the systems are allowed to dry. Non-coulombic interactions may be more important for interactions between silanol surfaces and humic and fulvic acids. Our lack of complete knowledge of the constitution of humic and fulvic acids and our limited knowledge of the nature of the surfaces of clay particles in soils hampers our understanding of the interaction between clays and organic compounds in soils. The adsorption of well-defined organic materials by montmorillonite has been extensively used to model the interaction between clays and organic compounds. Surfaces of hydrous oxides are probably at least as important as mica-type surfaces in many soils. Adsorption behaviour at a montmorillonite surface may differ considerably from behaviour at the hydroxylic surfaces of such materials. There is a need for much further work on the occurrence and characteristics of hydrous oxides and poorly related or non-crystalline materials in soils. Such materials' interaction with anionic organic materials merits further detailed study (Greenland, 1971).

Interest in the organo-mineral derivatives of humic acid has developed because of the major role that this group of compounds plays in the migration and accumulation of substances in the soil profile and in the biogeochemical transformation of substances in the earth's crust. The extensive material published during the last few years on the characteristics of these compounds has thrown light on some of the most important aspects of this problem. The earliest classifications of the organo-mineral derivatives of humic acid were proposed in the 1930s by Springer (19360, Tyurin (1937) and Tyulin (1937). In the 1940s, Antipov-Karatayev et al. (1948) published their experimental investigation, which included a more detailed grouping of the products of the interaction of the humic acids and the components of the mineral part of the soil. All the schemes were experimentally supported by the fractionation of the soil humus and by studies on the properties of their salts with strong bases (Alexandrova, 1967).

The present stage in the study of the organo-mineral derivatives of humic acid started in the 1950s, a period characterised by broad experimental research on the artificial preparation of iron- and aluminium-humus derivatives, their isolation from soils, and the study of their nature and properties. Mention must be made of the works of Bremner and Lees (1949), Alexandrova (1954), Kukharenko (1946), Manskaya et al. (1958, 1964), Schnitzer and Skinner (1964), Wright and Schnitzer (1963), Kononova et al. (1964). Alexandrova (1958, 1960 suggested that three groups of these compounds be distinguished: i) humates and fluvates of strong bases, ii) complex aluminium - and iron-humus compounds, and iii) products of their interaction with soil containing fractions with different particle sizes, Kononova (1963) cites the last classification proposed by Antipov-Karatayev, who also distinguishes three groups of these compounds: i) humates and fulvates, ii) complex compounds (chelates), and iii) adsorbing organo-mineral compounds "argillites", including the adsorbing compounds of humic acids with clay particles and the nonsilicate forms of sesquioxides. Classifying with the argillites (i.e., hardened clays) all the products of humus adsorption, including the nonsilicate forms of the sesquioxides, does not seem desirable. Tyurin proposed this term only for the products of the interaction of humus and clay. The nature of organo-clays presents an almost infinite variety of challenging problems. Although a voluminous literature on organo-clays has been built up during the past 20 years, the nature of soil organo-clay complexes is not fully understood. Earlier investigations on this subject have been mainly concerned with artificially prepared organo-clays and, in most cases, organo-montmorillonite complexes (Mortland, 1970).

Very few studies have been made on the nature of organo-clays in soils. Brydon and Sowden (1959) studied clay-humus complexes obtained using Tyulin's fractionation method. Some investigators (Chaudhury and Stevenson, 1957) showed that calcium, aluminium, and iron may be involved in the adsorption of humus on clay.

Clay minerals, particularly the fine colloids, with tremendous surface area and numerous reaction sites, adsorb organic constituents in such a way as to render the latter insoluble in common solvents. It has been reported that as much as 50% of the organic matter of mineral soils is unextractable by commonly used procedures (Stevenson et al., 1952). This fraction of organic matter is present in an insoluble or clay-adsorbed form or both.

2. REVIEW OF LITERATURE

Studies on clay-organic complexes could not make much headway primarily because of the nonavailability of a suitable, non-destructive method of isolating them. As a result, investigators preferred to study the properties of synthetic complexes or inorganic oxides of iron, aluminium and other cations with humic acid and fulvic acids. Work was also directed to studying clay mineral-oxide complexes and, to some extent, clay mineral-organic complexes.

The literature on the above studies has been reviewed and presented under four headings.

- a) Isolation of clay-organic complex;
- b) Clay-oxides complex;
- c) Interaction between inorganic and organic constituents and its effect on soil properties; and
- d) Naturally-occurring clay-organic complex.

2. a) Isolation of clay-organic complex

Apart from the complexity of the soil system, the main difficulty in such investigations has been the lack of methods of isolating clay-organic matter complexes in soils without seriously affecting the properties of these materials. Many new techniques and equipment are being introduced into soil laboratory practice on an ever-widening scale to make the laboratory work more efficient. One of these innovations is the use of ultrasonic generators, which up to this time have been used in soil science for accelerating physicochemical and chemical reactions in the study of sorption phenomena, on the one hand, and especially to disperse samples before particle size analysis, on the other. Ultrasound is currently used in numerous and very diverse areas of science and technology. The literature on this subject is extensive (El'piner, 1963; Crawford, 1954). These publications consider the dispersion effect in soil suspension chiefly as the result of cavitation and the phenomena that follow it in an ultrasonic sound.

Whittles (1923) was the first to demonstrate the powerful effect of sound waves on soil suspensions when he obtained an enormous increase in the number of free bacteria found on microscope plates prepared from sonified suspensions. Sonic vibration was compared with other physical methods of dispersion by Puri and Keen (1925), who saw the technique to be more effective than a rotary shaker but less effective than using a rubber pestle or shaking with glass beads. Wood and Loomis (1927), in a study of the physical and biological effects of high-frequency sound waves, found a "very difficult" soil sample provided by the N.S. Bureau of Soils was "completely dispersed in water within a few minutes". Olmstead (1931) used a large piezoelectric quartz crystal in an oil bath to vibrate suspensions of soils in dilute ammonium hydroxide solution contained in conical flasks. Unfortunately, the choice of soils was restricted to those with a high clay content and containing only small amounts of organic matter.

Also, his apparatus was expensive and difficult to construct or operate; consequently, there was a lapse of almost thirty years before ultrasonic dispersion of soils was studied again.

In the meantime, attention was mainly turned to the dispersion of finely ground minerals and clay particles. Sollner (1938) studied the dispersion of solids of low cohesion, such as mica, steatite, gypsum and graphite, and reported that ammonia was essential to prevent their coagulation. In contrast, using ammonia was deemed unnecessary by Mathieu-Sicaud and Lavavasseur (1949) when studying the effect of ultrasonic frequency on the dispersion of kaolinite and montmorillonite. Further, they found that maximum dispersion of kaolinite was obtained at a frequency of 900 KHz and montmorillonite at 320 KHz.

More recently, there has been renewed interest in ultrasonic dispersion of soils. Vasil'eva (1958) claimed that a greater yield of colloidal particles was obtained from clay soils by ultrasonic dispersion than by the "standard physicochemical methods". Barkoff (1960) confirmed this, who found 20-28% more clay size material in clay soil when subjected to ultrasonic vibration in a peptising solution of Calgon or Na₂CO₃ than when shaken with these reagents for five hours. Undoubtedly, the most important works are those of Edwards and Bremner (1965, 1976a) and Saly (1967), who have studied in detail the optimum conditions for the instruments they have used and, in addition, have investigated the effect of ultrasonic waves on various minerals in an attempt to recognise possible harmful effects on soil particles. Edwards and Bremner used a broad range of soils, the only obvious omissions being Andosols and gypseous soils, and both sonic and ultrasonic dispersion were studied. Further work has been reported by Vladimirov (1968), Bourget (1968), Boufils and Dupis (1969) and Watson (1970).

The methods of using ultrasonics are quite varied. The apparatus and its characteristics are variable, and the intensity of ultrasonics used, the suspensions' concentration, stabilization, and exposure times are also different. The vessels (size and material) in which the samples are also exposed to the vibration vary. There is general agreement in the literature that using ultrasonics produces very effective dispersion in a relatively short time. As regards the extremely important question of whether using ultrasonics destroys the crystalline lattices of minerals and the breakdown of the primary grains, there is still no general agreement. Some authors state either directly (Crowley and Welch, 1954; Matthiat, 1964) or indirectly (Medvedeva and Sergeyev, 1963; Wetzel, 1951) that destruction does not occur even with prolonged exposure, while others (Shutov *et al.*, 1961, 1962; Cita, 1964) hold that destruction starts when the exposure lasts more than 5 minutes 9saly, 1967).

The work reported by Edwards and Bremner (1967a) originated from studies of the effects of sonic and ultrasonic vibration on the extraction of organic matter from soils by 0.1 M Na₄P₂O₇ and 0.5 M NaOH. Felbeck (1959) reported that the amounts of organic matter extracted by treatment of soils with these reagents for three hours were increased by 20-48% if the soil reagents suspensions were subjected to ultrasonic (40 Kc) vibration. Edwards and Bremner conformed this observation but found that the amounts of organic matter extracted by shaking soils with these reagents for twenty-four hours were not markedly affected if the soil reagent suspensions were subjected to sonic (9 Kc) or ultrasonic

(18- 20 Kc) vibration for one hour before shaking and were not increased significantly if the soils were suspended in water and subjected to sonic or ultrasonic vibration for one hour before treatment with alkali or pyrophosphate. However, visual observations showed that sonic or ultrasonic vibration of soil-water suspensions caused considerable dispersion of soil particles and that the vibrated suspensions had high stability. This led the authors to suggest that it might be possible to disperse soils effectively by sonic or ultrasonic vibration of soil-water suspensions, thereby eliminating the treatments with oxidizing agents, acids and peptizing reagents considered necessary to achieve complete dispersion.

The findings of Edwards and Bremner (1967a) can be summarized as follows:

- a) The vibration technique points to the complete dispersion of soil particles without using oxidants, acids, or peptizing reagents. It is effective with highly calcareous soils, Latosols and soils containing large amounts of montmorillonite and organic matter, and it yields stable suspensions. It does not cause the dissolution of significant amounts of organic or inorganic material and permits the isolation of the clay-organic matter complexes in soils.
- b) Microaggregates () > 250 μ diameter) are rapidly disrupted by vibration, and primary sand particles are separated very rapidly from other soil particles by these treatments (e.g. by sonic vibration for 1-4 minutes).
- c) The vibration method of dispersion is more effective than the customary peroxide-Calgon methods. The dispersion achieved by shaking soils with Calgon solution after treatment with hydrogen peroxide is largely due to the destruction of organic matter in the peroxide treatment and subsequent shaking with water, the Calgon having comparatively little effect.

The ultrasonic vibration provides a means of dispersing soil particles in water in the absence or chemical reagents (Watson, 1971) and, therefore, reduces the risk of chemically changing soil material during vibration. This technique was used by Watson and Parsons (1974) in their investigation of nitrogen components present in the fractions of organic mineral complexes from several soils.

Major considerations in using an ultrasonic probe in soil dispersion are the duration of treatment required and the ability to reproduce power output. Edwards and Bremner (1967a, b), among others, have noted the substantial heat build-up in suspension undergoing ultrasonic dispersion. With the sonic probe, this was found to be rapid in the first 10 minutes, but temperature increases were insignificant after 20 minutes of insonation. Thus, temperature control using a water jacket is recommended to minimise hydrolytic or other changes in soil constituents during bulk isolation of soil separates.

The increase in temperature during sonification was due to the generation of heat due to sound absorption in the exposed liquid. The different specific heats of the solution are the reason for the temperature differences. During exposure to ultrasonics for 5 min, the temperature rose by 17 ^oC and, in some cases, by 53 ^oC. The suspension heated up more, the denser it was and the greater the intensity of the ultrasonics. The influence of concentration is apparent above all other factors in using ultrasonics with weak dispersing action at a frequency of 1 MHz and in the dispersing affect produced in water.

The lower the concentration, the more complete the dispersion. Out of the 30 different experimental combinations, in 21 cases (70%), the highest content of particles smaller than 0.01 mm in diameter was observed at a concentration of 2.5%. This is because a suspension of lower concentration absorbs the sound energy less effectively, so the cavitation effect is less pronounced (Saly, 1967).

A literature review indicates that the frequency of the sound is important to dispersion, and according to certain authors, the influence of frequency is critical (Mathieu-Sicaud and Levavasseur, 1948). Keeping the size of the sample, the quantity of dispersing substance, the volume of the suspension, and the exposure time (4 minutes) to ultrasonics the same, it was concluded that the dispersion effect of ultrasonics at low frequencies is most effective and that the extent of dispersion also increases with increasing sound intensity.

Based on Saly's (1967) work, it can be stated that ultrasonic acts mechanically on soil particles and that the destruction of the soil aggregates limits this effect. A very important consequence of ultrasonics is the separation of small, chiefly colloidal particles from the silt and sand particles. Cleaning the surface of larger soil particles is relatively complete and much better than other dispersion methods. Destruction of primary particles was no longer extensive with ultrasonics exposure for 5 minutes. There is still some question about the destructive effect of prolonged exposure to ultrasonics (more than 15-20 minutes or more, perhaps in the case of montmorillonite) since, given the forces of hydraulic shocks, one cannot exclude the possibility of cavitational erosion. However, this does not involve exposure to vibration for up to 5 minutes, according to the data published by Saly (1967).

In the methods of dispersion (shaking, boiling, etc.) used up to the present time, there is no clear concept of the consequences to which they lead. In this case, one cannot eliminate the possibility of destructive action on the elementary particle, especially if it breaks down during weathering. Experiments carried out by different workers quite convincingly show that ultrasonics as an element of a new method of dispersion has no drawbacks compared with other methods. Still, rather, it has several noteworthy advantages.

The published literature has confirmed that different ultrasonic generators have different dispersion effects. The degree of dispersion depends on the nature of the soil particles themselves. Given the broad variation in soil composition as well as the fact that this composition is not known ahead of time, it is impossible to choose a specific sound-exposure regime for each case, just as in other methods of dispersion, it is impossible to take into account consistently the individual differences and requirements of individual samples. It is necessary to choose a combination which would provide dispersion even in the case of very tightly cemented aggregates. The need for comparability of results obtained in different laboratories presupposes standardization of methods, which also applies to the technology and the laboratory procedures.

Many soil scientists have recently believed that removing humus, sesquioxides and calcium carbonate from the soil before making a particle size analysis is undesirable and pointless. Just as the silicates, the carbonates are equally important components of aggregates, and they must be considered in the particular group of separate in which they naturally occur.

It was proposed by Saly (1967) that exposure to ultrasonic only in distilled water is insufficient since even though dispersion occurs, the colloidal particles again flocculate later. Thus, a dispersing substance must be added to stabilize the suspension and adjust the pH, which often changes with exposure to vibration. The pH changes during ultrasonic exposure due to nitric acids or H_2O_2 formation. The pH deviations could be reduced after adding hexametaphosphate because of its buffering action.

The dispersion efficiency of ultrasonic vibration of Gleysolic soil samples in water or in electrolytes was compared to that obtained by the peroxide-Calgon method, with insonation in electrolytes yielding generally higher recoveries of clay than insonation in water. Ultrasonic dispersion in water was accomplished by considerable dissolution of Fe, Al, Si and organic carbon. At the same time, 0.01 M BaCl₂ or 0.1 M NaCl resulted in substantial suppression of these dissolution effects, with CaCl2 being the most effective (Hinds and Lowe, 1980). While the variation in results for these elements is not easily explained, it is suggested that lower values of soluble basic cations resulting from dispersion (as compared to those from shaking treatments) may be partly due to exposure, by ultrasonic treatment, of additional cation exchange sites permitting further ion exchange reactions. The possibility was considered that pH changes resulting from ultrasonic treatment might influence the dissolution effects. Ultrasonic dispersion of the 10 samples gave small but consistent increases in pH, averaging from 0.28 pH units, with a range of 0.1-0.5 pH units. While decreasing pH might well increase solubilization, particularly Fe and Al, small increases (within the pH range of 5-7) are not likely to account for the increased dissolution of Fe, Al and Si observed. However, additional work will be needed to establish whether the observed "suppression" is due strictly to the prevention of dissolution or to dissolution similar to that in water, followed by secondary adsorption or precipitation reaction. As the results indicate that ultrasonic dispersion of Gleysolic soils in electrolytes rather than in water has the advantages of better dispersion, more yield of clay and less alteration of organo-mineral complexes during isolation, the authors (Hinds and Lowe, 1980) recommended carrying out dispersion in electrolyte medium, preferably CaCl₂ because such procedures should be of particular value in bulk isolation of particle size separates, where subsequent characterization or mineralization studies of organo-mineral complexes are to be undertaken.

Although ultrasonic vibration is a quick and highly effective method of soil dispersion, sideeffects on soil constituents may well be greatly enhanced because of the high energy involved. Coarse particles are undoubtedly susceptible to breakdown for less and is usually recovered from ultrasonically dispersed samples. Adams and Stewart (1969) estimated the abrasion of sand grains in soils derived from sedimentary rocks by comparing the effects of ultrasonic vibration on fine sand-sized soil particles. However, clay and organic matter in most soils will undoubtedly "buffer" the abrasion of coarse particles to some extent. The abrasive effects on soil minerals were studied by Edwards and Bremner (1967a), who found that fragile minerals, such as biotite, were more easily abraded by sonic vibration than by shaking in water. For most minerals, however, sonic vibration for up to one hour was slightly less abrasive than 10 hours, water-shaking and significantly less damaging to fine particles than treatment with H_2O_2 followed by shaking with Calgon. By comparing electron micrographs of sonified (25 KHz) and non-sonified Na-montmorillonite suspensions, Robertson *et al.* (1968) showed that ultrasonic vibration caused the breakdown of the microaggregates into thin flakes after only one minute; longer treatment (15 minutes) gave smaller flakes, indicating further breakdown.

Several workers have investigated possible "cavitational erosion" of clay minerals. Three stages have been recognised. First, contaminants may be removed from external surfaces, as Koms'ka et al. (1966) observed for kaolinite. A second stage was performed by Gata (1964), which involved splitting the original clay lattice, accompanied by increased cation exchange capacity and vibrations in X-ray diffraction patterns. Finally, complete fragmentation of the existing structure and a regrouping of the freshly formed surfaces into new mineral aggregates have been observed by Kruglitskii *et al.* (1966). Although the latter workers have produced several papers (in Russian) on clay mineral alterations, only limited details are given in the available English abstracts, and the results might well be treated with caution (Watson, 1971). As Saly (1967) points out, there is certainly no general agreement on the importance of cavitational erosion and clay fraction isolated by Watson (1970) after ultrasonic dispersion showed typical X-ray diffraction peaks and IR spectra. Presumably, structural alterations become serious only in well-characterized minerals free of associated organic matter and other amorphous material and subjected to a high ultrasonic intensity.

There is, however, one important question which remains as yet unanswered: the extent to which ultrasonic waves modify soil organic matter, physically and chemically. In addition to causing an increase in suspension temperature, ultrasonic vibration may promote several types of chemical reactions within a liquid medium- oxidation, reduction, hydrolysis, free radical polymerisation, depolymerisation, molecular rearrangements and photochemical reactions. There is a vast amount of literature on each type of reaction (El'Piner, 1964), and only a few examples can be quoted here. It should, however, be mentioned that most sonochemical studies have involved pure reagents, and often, only trace amounts of products are formed. One sonochemical reaction of practical importance is the precipitation of free iodine from aqueous KI in the presence of carbon tetrachloride (Kusano, 1936; Weisser *et al...*, 1950) for the iodine can be titrated with standard sodium thiosulphate solution (Hughes, 1961) Not withstanding these observations sonification appears to be the only safe way of isolating clay-organic complexes from soils.

2. b) Clay-oxides complex

It is generally believed that oxides reside on or are bonded to surfaces of other soil minerals of various particle sizes. This cements 'active' particles and changes the surface properties if the particles are charged. Indirect evidence of this interaction has often been presented through a change of charge characteristics and aggregation after removing synthetic oxides from, or in addition to, soils or clay

minerals. However, extraction procedures (such as CBD) are never strictly specific for a certain oxide, nor were the oxides added to or formed in the presence of other soil constituents necessarily identical with their pedogenic analogues, mainly because of different formation conditions. Therefore, more direct evidence of the interaction is necessary, and recent studies combining high magnification electron microscopy with electron microscopic analysis appear promising in so far as learning more about these interactions is concerned (Fordham and Norrish, 1979).

Not much is known about the different affinities of the various oxides for the surfaces of other minerals, especially clay silicates. Because of their relatively lower tendency for hydrolysis in solution, Al-oxides can pertain to positive charges in the acid pH range of soils; therefore, they can be adsorbed at the surface of clay minerals and neutralise negative layer charges. On the other hand, Fe-oxides do not develop coulombic positive charges in soils' generally prevailing pH range because of their much higher tendency to fully hydrolyse. For their retention by soil components, forces other than coulombic ones might be of greater importance. Electron microscopy, however, very often shows that Fe-oxides exist as separate micronodules and are not associated with clean kaolinite crystals (Kampf, 1981). Nothing is known about the situation of Ti and Mn-oxides in this respect.

Through the adsorption of oxides on the surfaces of other soil minerals, the surface properties of both components will change in magnitude and possibly also in character through mutual neutralization or interaction. Oxic soils may lose most of their (naturally low) permanent charge and, consequently, their ability to retain cations essential for plant nutrition (Schwertmann and Taylor, 1982).

Dochaufour (1963) studied the role of iron in organo-mineral complexes. Humic compounds and their Fe contents were determined, and the Fe content in the complexes and the free form were calculated in ten different types of humus. Fulvic acids abounded in acid humin, brown humic acids predominated in the B horizon of podzol, and highly polymerized grey humic acids were highest in media rich in Ca (Rendzina). Complexed Fe (dissolved together with humic acids in an alkaline medium and precipitating in a highly acid medium), as compared with free Fe, was low in forest mulls and rendzinas and was high in other humus types indicating a direct relationship between the complexing of Fe and the degree of humification. The Fe complexed by fulvic acids is mobile (Podzols) and that by humic acids is insoluble, forming unstable complexes.

Kuznicki and Sklodowski (1969) studied the effect of soil-forming processes on iron and aluminium contents of organic-mineral complexes. Humic complexes of Al and Fe in several soil profiles were investigated. They found the amounts of Al and Fe bound to various humic compounds, and their mobility depended on parent material as well as on the degree of weathering in addition to alteration of organic matter in the course of soil formation. Consequently, the Al and Fe contents of the light and heavy fractions of humic matter were related to soil type.

Complexes of Fe- and Al-humus compounds were extracted from soils by $0.1 \text{ N Na}_4\text{P}_2\text{O}_7$. The forms in which Fe and Al were complexed were indicated by the ratio of (Fe + Al) to C and were different in a shallow podzol, a dermo-moderately podzolic soil, and a thick and a shallow chernozem.

At (Fe + Al): C ratio < 0.3both Fe and Al were present in ionic form. At ratios of 0.3-0.5, Fe remained in ionic form, but Al was present as Al $(OH)^+_{2}$, and at ratios of 0.5-1.0, both metals existed in the M(OH)₂ form (Kononova and Bel'Chikova, 1972).

Iron chelate of some simple di- and trihydric phenols can be decomposed by peroxide treatment or by hydrolysis to yield crystalline ferric oxides. The species of ferric oxide obtained depends upon the precipitating conditions and nature of the chelating ligand. In oxidative, virtually anion-free conditions, decompositions of all aged chelates yield a precipitate of disordered ferric oxide, which is referred to as "protohematite" since it goes to hematite in water even at room temperature. Protohematite is considered a discrete form of ferric oxide similar in structure to ð -FeOOH but devoid of hydroxyl groups and may be present in freely drained soils as a precursor of hematite. Hydrolysis of all unaged chelates, except that of iron protocatecharic acid, yields lepidocrocite. The redox cycle undergone by iron in this reaction may be analogous to one prevailing in gley soils. In the presence of montmorillonite, the iron-catechol system forms a clay-metal-organic complex, which also decomposes to yield lepidocrocite, provided chloride ions are present on the clay surface. The fact that various inorganic gels amorphous to X-rays can also deplete the ligand content of the chelates indicates a possible inorganic decomposition mechanism for metal-organic chelates in soils (McHardy *et al.*, 1974).

Investigation of metal-organic complexes by chemical, IR-spectrophotometric, thermal and Xray methods revealed that 22-.8 and 70.4% of the soil C was in the purified complexes. The most prominent metal in all complexes was Al, which constituted between 3.45 and 7.17% of the air-dry weights. Other major inorganic constituents were Fe and Si. The Al and Fe in the metal-organic complexes appeared present as Al (OH)²⁺ and Fe (OH)²⁺ bonded to negatively charged carboxyl and phenolic hydroxyl groups on the ligands. X-ray analysis failed to show any crystallinity in the complexes. After removing most of the metals, the ligands were identified as fulvic acids (Griffith and Schnitzer, 1975).

The crystallization of goethite and hematite from aqueous suspensions of ferrihydrite and of ferric oxides from Fe (III)-fulvic acid (FA) complexes was studied by Kodama and Schnitzer (1977). The crystallization of Fe (III) oxides was mainly governed by the form of Fe (III) initially present and by the amount of FA present. When Fe (III) was present as ferrihydrite, crystallization depended on FA concentration and pH. Fa concentrations of 0.5 g/l favoured the crystallization of hematite rather than goethite, but 5 g/l completely inhibited crystallization. Increasing the pH from 4 to 10 tended to favour crystallization. When Fe (III) was present as FE (III) -FA complexes, crystallization of oxides rarely occurred. Failure to detect large amounts of crystalline oxides in soils developed under cool temperate climates., despite high total Fe levels is partly due to the adsorption of FA and other organic materials on ferrihydrite surfaces and to the presence of Fe-organic complexes.

Ubogov (1978) studied the effect of iron and aluminium on precipitation of the humus-clay complex. The peptization and swelling of the organo-mineral complexes were obtained when bentonite was saturated with Na-humate and various forms of Al and Fe. Ionic forms of Al and Fe produced stable

complexes; the resistance towards the peptizing action of water was maintained when they were saturated with Na up to 40% of the adsorption capacity. Sesquioxide sols from solonetzes did not form organo-mineral complexes resistant to peptization.

Acetylacetone in benzene has been found to extract fractions of soil Fe and Al without removing organic matter. A comparison of this extractant with acetylacetone in water and with classical reagents for Al and Fe indicated that metals extracted by acetylacetone in benzene are essentially bound to the organic matter. The method leaves the residual soil well aggregated, but when treated with water, the aggregates lose coherence. Five Italian soils showed similar true-course patterns for both extraction of metals and the percentage decreases in water-stable aggregates (>0.2 mm). The metals behave as a junction of a net of polymeric chains of organic matter (Giovanni and Sequi, 1978).

Organo-metallic complexes between fulvic acid (FA) and Al were studied *in vitro* and in undisturbed soil samples. Pseodosoluble complexes are formed between FA and Al^{3+} , $Al (OH)^{2+}$ and $Al (OH)_{2}^{+}$ ions; FA also forms dispersed or flocculated association with Al hydroxide. Complexes with Al $(OH)^{2+}$ and $Al (OH)_{2}^{++}$ are formed only by alkaline ions. In the presence of Ca, mobile complexes with Al^{3+} are transformed into unstable dispersed colloidal associations. These colloidal associations are a form of Al storage and have been identified in B horizon pf podzols (Dupis et al., 1979).

Mossbauer spectroscopy has been used to provide information on the effect of pH on the nature of the complexes formed between iron and humic acid. Iron occurs in the ferric form at an initial suspension pH greater than three. However, assessing how much it combines with organic matter isn't easy. On lowering the pH, iron is reduced with a considerable proportion of the ferrous iron entering the solution, partly as a solved iron and partly as complex forms. Raising the pH leads to reoxidation and the precipitation of a considerable proportion of the iron in an inorganic form with Mossbauer parameters similar to those or β -FeOOH. No evidence was obtained for Fe (III) in solution or for Fe (II) in any form at pH values greater than 4 (Goodman and Chesire, 1979).

⁵⁷Fe Mossbauer spectra of samples of HA, FA and Kerogen and the organic material extracted from bituminous chalk with benzene-methanol indicated that iron occurred in a trivalent residue of the HA fraction, as hydrated ferrous ions in the FA fraction, as pyrite in Kerogen and a form not detectable by Mossbauer spectroscopy in the benzene-methanol extract (Dickson *et al.*., 1979).

Organo-ferric and organo-aluminic complexes were studied in a toposequence of soils over granite comprising a brown ranker, an Atlantic ranker and a humic fluvisol, all rich in organic matter and sesquioxides, under a mixed vegetation of healthier pine, Gramineae and Leguminosae. The complexing capacity of the organic matter of these soils ranges from 17-550 Fe/g C, and from 32 to 750 mg Al/g C. The complexing capacity of the humic acid ranges from 4-99 mg Fe/g C and 8-520 g Al/g C, while values found for fulvic acids are 36-984 mg Fe/g C and > 1 g Al/g C. The predominance of humus-Al-complexes over humus-Fe-complexes explains the persistence of the organic matter in the profile and the presence of a high level of insoluble components easily extracted with alkaline reagents (Carballas *et al.*, 1980).

Most of the extractable organic matter in an Umbric Dystrochrepts occurred in the microaggregates fraction (< 50 μ); 65-70% of the extractable organic matter was weakly attached by electrostatic bonds to the surfaces of the microaggregates in the form of mobile complexes. It is mainly comprised of humic acids, with metal content dominated by Fe on the surface horizons and Al on the lower horizons. Nearly 20-25% of the extractable organic matter was directly bound to the clay utilizing a bridging complexed cation.

Fulvic acids predominated, especially in subsurface horizons. The principal binding cation was Fe, although Al was also present in small amounts. The metal content of these immobile complexes was high. Nearly 5-10% of the exactable organic matter was adsorbed in amorphous Al-polymers and comprised principally of humic acids (Gonzalez and Fuente, 1980).

Marok (1980) carried out potentiometric titration of aluminium uromide and aluminium humic acid systems and found that aluminium formed complexes with glutamic acid, galacturonic acid, and humic acids. A similarity of reactions between AlCl₃ and humic acids on one hand and AlCl₃ and glutamic acid on the other suggested that humic acids contained polyuronides similar to those used artificially. Aluminium formed soluble complexes with humic acids.

Some of the factors controlling Al-humate bonding, a major aspect of organo-mineral interactions in soils, were studied by Arai and Kumada (1981). The methods used were potentiometric titration and stability measurement. The samples comprised four humic acids plus two polyuronic and several monomeric carboxylic acids as model compounds. Humic acids and alginic and polyacrylic acids were shown to form complexes with Al. The stability of Al humate complexes was shown to be controlled by the polymerization of carboxyl-containing units and by the arrangement of carboxyl groups in the units. Fluorescence excitation spectra of FA and its Cu and Fe complexes showed that fluorophore groups participated in metal complexation with a concomitant reduction in fluorescence intensities. The two characteristic bands at 360 and 465 nm were affected by complexation, but in addition, the 360 nm band shifted gradually towards longer wavelengths as more metal was complexed. Viscosity measurements indicated a decrease in FA's molecular flexibility with increasing metal complexing. This rigidity or string in the structure was ascribed to metal complexing with carboxyl and phenolic hydroxyl groups, bringing the macromolecular segments closer. Viscosity and average molecular weights also increased as more metal was complexed, possibly because of the formation of metal bridges between Fa molecules. The two effects mentioned above were more prominent at pH 6.0 than at 4.0. The flexibility of FA molecules at pH 6.0 is greater than at pH 4.0 because of a reduction in intra-molecular H-bonding at the higher pH, which allows the Fa to interact with metal ions more favourably (Ghosh and Schnitzer, 1981).

Greenland (1971) stated the it seemed probable that hydrous oxides were likely to provide more sites for organic matter adsorption in soils than the surfaces of micaceous clay minerals. Considerable speculation exists about the occurrence of hydrous oxides in soils, particularly the amount present as non-crystalline gels and as coatings on the surfaces of clay minerals (Greenland and Wilkinson, 1969; Mitchell et al., 1964). Crystalline oxides of iron, aluminium, and silicon are well known to be widely distributed in soils, and they have surfaces that are normally hydrated so that they can participate in adsorption reactions similar to those of hydrous oxides. However, they usually occur as crystals of relatively large size and hence limited "activity". Non-crystalline hydrous oxides have very extensive and active surfaces. However, such hydrous oxides are unstable and revert relatively rapidly to more stable crystalline forms. Under laboratory conditions, this "ageing" process usually takes a few months to a few years (Mackenzie and Maldau, 1959; Schnitzer, 1969). Thus, they might only be expected to occur in large amounts in very young soil or where periodic changes in soil conditions cause iron, aluminium or silicon to be brought into solution and later reprecipitated in the active form. However, Schwertmann and his associates (1965,1966) have found that the amounts of non-crystalline iron hydroxides in soils are greater than would be expected from laboratory studies on the crystallization of such materials in relatively pure systems and subsequently shown (Schwertmann et al., 1968) that noncrystalline ferric hydroxide gels are exceptionally stable in the presence of soil organic matter, and citrate ion. He suggests that the sorption of organic ions is responsible for the stability of non-crystalline iron-hydroxides in soils. It is probable that the sorption of organic anions is also responsible for the fact that "free iron oxides" in many surface soils do not appear to carry a positive charge (Deshpande et al., 1964).

Non-crystalline iron hydroxides may be expected to occur in situations where they are freshly formed and where the sorption of organic materials stabilises them. Such conditions will include those where the soil is subject to seasonal flooding, podzol B horizons and those where the soil contains actively weathering iron-rich minerals (Oades, 1964).

The occurrence and distribution of non-crystalline aluminium hydroxides in soils is still inadequately understood. Part of the difficulty is the lack of any suitable methods for their recognition. Twenboah et al. (1967) have suggested that aluminium brought into solution in 12 hours at room temperature, when the soil is shaken with 1 M calcium chloride at pH 1.5, provides an approximate measure of such material. Results obtained by this technique indicate a rather widespread occurrence of non-crystalline aluminium hydroxides in slightly acid soils. The recognition of aluminium hydroxide interlayers in expanding lattice clays in many soils (Rich, 1967) indicates that aluminium hydroxide can be precipitated in such soils. It seems very probable that aluminium "outer layers" and interlayers are common in acid conditions.

Where clay minerals are coated with "outerlayers" of hydrous oxides, their surface reactions will be those of the hydrous oxide, not the clay. It is, therefore, important to know when and where they occur. Again, the useful information on this point is less than desirable (Greenland, 1971). Surface coatings of iron hydroxides on clay particles can be formed by precipitation under acid conditions (Follett, 1965; Greenland and Oades, 1968). Although such coatings do not seem to exist on the kaolinite particles of many lateritic soils (Greenland *et al.*, 1968), non-crystalline iron hydroxides occur in certain soil conditions when the clay particles become embedded in the gel. Surface coatings of poorly ordered material have been observed on the clay particles of redbrown earth in Australia (Greenland and Wilkinson, 1969) and subsequently on several other Australian soils. These crusts are removed by treatment with 5% sodium carbonate (Follett *et al.*, 1965), indicating a similarity to allophane. However, differential infra-red spectroscopy (Wada and Greenland, 1970) suggests they have a more ordered structure than allophane. There is need for considerable care in the designation of such surface coatings.

Reactions between organic matter extracted from the Bh horizon of a podzol and the metal ions Fe⁺⁺⁺, Al⁺⁺⁺, Ca⁺⁺, Cu⁺⁺ and Ni⁺ were investigated by potentiometric and conductometric titrations, adsorption, IR spectroscopy and flocculation experiments. One formed stable water-soluble complexes with all the metals over the pH range usually found in podzols. The Fe⁺⁺⁺, Al^{++,} and Cu⁺⁺ ions formed a soluble 1:1 molar complex with organic matter at about pH 3, and Fe⁺⁺⁺, Cu⁺⁺ and Ca⁺⁺ formed a 2:1 molar water-soluble complex with organic matter at pH 5. There were indications of a water-insoluble 6:1 molar complex formation between Fe⁺⁺⁺, Al⁺⁺⁺, and organic matter involving the COOH group per metal atom in each instance. There was evidence of the formation of electrovalent bonds between negatively charged carboxyl groups of the origin matter and positively charged partially hydroxylated Fe and Al compounds. There was no clear indication of the participation of phenolic OH groups in the organo-metallic reaction. The data show the uptake by organic matter of Fe from goethite after standing under air or N, shaking under air or N, intermittent leaching or perfusion; the uptake of Al from gibbsite after standing or shaking under air, or intermittent leaching; Fe and Al uptake from metal-enriched exchange resins and soil; Fe uptake of untreated and methylated organic matter. After continuous wetting and leaching in a perfusion apparatus for 1 week, 1.0 mol organic matter mobilized 1.0 mol of Fe from goethite and the Fe-saturated exchange resin and 1:1 mol of Al from the Al-saturated exchange resin. After standing and shaking, metal uptake was considerably lower after intermittent leaching. The atmosphere (under air or N) had no apparent effect of Fe uptake by organic matter. Methylation of most of the active acid groups reduced Fe uptake to very low values, thus showing the important role of carboxyl groups in organic metallic reactions (Schnitzer and Skinner, 1963a, b).

DTA, DTG and isothermal decomposition studies were conducted on untreated fulvic acid and Na-montmorillonite, a physical mixture of the two, and on two complexes. The DTA curve of the in heated complex a major exotherm at 670 ^oC, indicating an interlamellar complex. Almost all the externally adsorbed acid decomposed before the combustion of the interlamellar retained acid. About half of the adsorbed fulvic acid was held externally (Kodama and Schnitzer, 1969).

While investigating the chemico-mineralogical composition of pre-colloidal and colloidal fractions of solodized soils of the OK-Don lowland, Akhtrytsev and his associates (1970) found that the colloidal complex of meadow-chernozem wooded steppe solonetz is an Mg-organo-Fe-Al-Si-complex in all the genetic horizons. In bog-meadow solod and dark grey forest colonized soil, the colloidal complex has been largely destroyed in the eluvial horizons, where it is an Mg-Fe-Al-organo-Si-complex, with a considerable admixture of biogenically accumulated elements; in the other horizons, it

is similar to the solonetz type. The colloids consist of montmorillonite, hydromica, kaolinite, chlorite, and quartz.

The molecular weight distribution of humic substances of the peat type and their complexes with bivalent (Cu^{2+} , Zn^{2+}) and trivalent (Al^{3+} , Fe^{3+}) metals was investigated by Kribek et al. (1977) using gel filtration. In all cases, the molecular weights of the complexes were higher than that of the humic substance; a reduction in the low molecular weight fraction accomplished this change. In these complexes, the metals are bound to the highest molecular weight fraction of the humic polymer. After the acid treatment of the complexes, the elation curve of the bivalent metal complexes showed the reappearance of a low molecular weight fraction. This indicates the stronger binding of trivalent metals to humic substances and their non-ionic nature.

Wada and Teruo (1976) extracted thirty-three samples of Ando soils with sodium pyrophosphate (0.1 M; pH 10) and dithionite-citrate. The Fe, Al, and C contents of these two extracts offer a means of differentiation in the status of humus about Al and Fe on different horizons. The humus that forms at first in the A1 horizon has a very low complexing ability for Al and Fe, and little is dissolved by pyrophosphate. The humus evolves with time or pedogenesis into forms that complex Al and Fe released from volcanic ash by weathering and which are dissolved by pyrophosphate. In the old horizons, the humus reacts with additional Al and Fe, some of which may be as hydrous oxides or allophane-like constituents, allophane and imogolite. This reaction probably makes the humus less soluble in pyrophosphate.

Adhikari and his co-workers (1972) fractionated fulvic acid complexes with Fe, Al, Cu, Zn and Ni from the organic matter of alluvial soil and studied their stabilities. Jambu *et al.* (1972), in their study of some aspects of iron fixation by humic acids, added FeCl₃ solution to humic acids dissolved in 0.2 N NaOH, which resulted in the formation either of pseudo soluble colloidal complexes containing up to 800 meq Fe/100 g of humic acids or flocculated material containing a higher proportion of Fe. DTA data indicated the existence of one ferrous and two ferric complexes in the materials.

Stability constants for complexes formed between humic acids and Cu are tabulated for several pH values of the reaction media. Complex formation at low appeared to involve undissolved acidic functional groups (carboxylic and possibly strongly acidic phenolic hydroxyls), and at high pH, the carboxylate ion (- COO^{-}), its enolate ion (- O^{-}) and possibly other donors (-OH, - NH_2 , -C=) (Krystanov, 1972).

A study of synthetic Fe-fulvic acid complexes showed that their solubility varied with pH and the amount of metal present. Precipitation occurred at pH 2.5-3.5 when the concentration of Fe reached 50 mg/g C. Peptization occurred at pH 7.0-9.8, and destruction of the complexes at pH values > 9.8 (Buckert and Metche, 1972).

Paired soils of high and low organic matter content from the East Anglian silts were used to determine the role of different organic constituents and complexed metal ions about aggregate stability. Although leaching with periodate and borate caused some loss of stability for most of the soils, the

changes were much less than those due to extraction with pyrophosphate or acetylacetone, which were more effective in removing organic materials complexed with Fe and Al. Amounts of Fe and Al extracted were not well correlated with changes in stability. The results indicate that polysaccharides are less important for aggregate stability in these soils than organic matter bonded to the clay particles through associations with Al or Fe (Hamblin and Greenland, 1977).

The chemical and spectral (IR) characteristics of complexes between humic acids and cations are described, and the sorption of phosphate by these complexes is studied by Cegarra *et al.* (1978). Under the experimental conditions (pH 4.0), the same type of bonds were operative in complexes formed with Ca, Al or Fe, salt linkages being the most important. However, OH-groups also played a significant part, particularly in complexes, depending on the type and concentration of the cations present, being small for Ca (1 me/ 100 g) and increasing to 96-241 me/100 g, for Al and Fe, respectively.

A solution of phenolic compounds was added separately to montmorillonite, illite and kaolinite, each of which had been mixed with quartz in a 3:7 ratio, and tom pure quartz. The oxidative polymerization occurred immediately and was allowed to proceed for 10 days. The humic and fulvic acids were found largely in montmorillonite and illite and much less in kaolinite and quartz. Their IR spectra resemble those of natural products. Their experiment also showed that the clay minerals and quartz catalyse the oxidative polymerization of pyrogallol. Contaminated FE and Al bear significant correlation with the catalysis. Among the minerals tested, the catalytic oxidation power decreases in the following order: 2:2 > 2:1 > 1:1 > quartz. The organomineral complexes formed were darker in colour when 2:2 and 2:1 minerals were used, particularly in the presence of contaminated Fe and Al (Wang *et al.*, 1978)

Karichev (1979) reported that the complexity of the chemical composition and the properties of polydispersed systems of organic substances determines the ratio of interacting components of watersoluble organo-iron complexes. Water-soluble organo-iron complexes' stability increases with the initial fractions' molecular mass.

Clay-humic (fulvic) acid complexes were produced by prolonged shaking of the compounds or by precipitation radiometry by adding different cations. While H, Na, K and Mg did not markedly stimulate the production of clay-organic -complexes, NH₄, Al, Ca, and Fe behaved as bridge cations (in increasing order) when montmorillonite was the clay mineral. Gradient elution, from neutral to alkaline, of synorogenic complexes showed the approximate percentage of the non-alkaline resistant cation bridge-type complexes, as well as the rate of formation of more resistant complexes associated with physical adsorption and SiOH linkages, Clay-organic complexes produced by direct hydrothermal synthesis, were more resistant than the cation bridge-type complexes. Electron microscopy showed a superficial coating of humus particles on the clay surface in the case of kaolinite and a more intrusive cloudy appearance in the case complexes of humic (fulvic) acid and montmorillonite or illite (Sharpenseel, 1966). Radiometric precipitation in a suspension of NH_4^- , tryptophane and histidinecoated montmorillonite in ¹⁴C labelled humic acid solution showed that the first two produced about the same high yield of clay-humic acid complex, whereas histidine gave a somewhat lower yield. Alkali extraction almost completely degraded montmorillonite-NH₄-humic acid complexes and decreased by 80% of the organic matter NH₄-N and total N contents in montmorillonite arginine-humic acid complexes. Ability to form complexes with humic acid and the stability of these complexes were compared for Fe-containing synthetic montmorillonite and complex of hydrothermally synthesized complexes of montmorillonite-¹⁴C humic acid; complexing power was highest in Fe-containing synthetic montmorillonia Fe³⁺. The coatings yielded an alkali-non-resistant ion-bridge. In all other complexes, the coupling of Fe occurred in the form of stable intermolecular bonding (Sharpenseel, 1968).

Using radiometric precipitation techniques and ¹⁴C-labelled materials, the effects of various amino acids on the formation of clay-humic complexes were compared. Tests with¹⁴C-amino acids and ⁵⁵Fe compounds, using double-labelled and either radiometric precipitation or thin-layer autoradiography, showed amino acids to be an effective as Fe in their ability to form clay-humic links, montmorillonite formed complexes more readily than kaolinite (Sharpenseel and Krause, 1972).

The interaction between 14C-labelled humic acids and montmorillonite saturated with different cations (H⁺, Ca²⁺, Fe³⁺) were studied. Amounts of humic acids adsorbed by unit weight or unit volume of the clay mineral were in the following order: Fe-montmorillonite > H-montmorillonite> camontmorillonite, indicating changes in adsorption energy with the different cations and stressing the important part played by Fe in the forming of organo-mineral complexes. Fe also had an important effect on flocculation; smaller amounts of organic matter were required for the flocculation of Fe-montmorillonite than that of H- or Ca-montmorillonite (Valla *et al.*, 1972).

Chen and Schnitzer (1976) investigated morphological features of humic substances. They reported that freeze-dried humic and fulvic acids were fibrous at pH 5.0 but had a fine granular structure at pH 10.0, with a range of intermediate structures at intermediate pHs. At low pH (2.0-3.0), fulvic acid occurs mainly as elongated fibres and bundles of fibres, forming a relatively open structure. With the increase in pH (4.0-7.0), the fibres tended to mesh into a finely woven network to yield a sponge-like structure. Above pH 7.0, a distinct change in structural arrangement and improved orientation was observed. At pH 8.0, the fulvic acid formed sheets, which tended to thicken at pH 9.0. At pH 10.0, fine, homogeneous grains were visible. The effect of pH on the humic acid structure was similar to that observed on fulvic acid, except that because of low solubility in water, the pH range had to be narrowed to between 6.0 and 10.0. The pH at which the major transition occurred was higher.

Appelt (1976) has proposed two possible interaction mechanisms between humic acid and allophanic soils. One potential mechanism is particle-particle interactions through coulombic attractions or non-specific adsorption, ligand-exchange or specific adsorption, hydrogen bonding and van der Waal forces. The other possible mechanism is the formation of complexes of humic compounds and. aluminium hydroxides and/or iron hydroxides ions that probably interact with surfaces of colloidal inorganic particles These mechanisms can operate simultaneously where the specific adsorption of

organic compounds could lead to the dissolution of Al from allophane and Al sesquioxides, favouring humic acid coagulation. Particle -particle interactions between these materialise seem to involve only the external surfaces, mainly because of steric hindrance, and the adsorption sites on the internal surfaces of both colloidal particles are available to react with ions which do not present steric hindrance. However, the discussion of the ions towards the reactive sites could be affected by the net charge resulting from the interactions between organic and inorganic colloids.

2. c)Interaction between inorganic and organic constituents and its effect on soil properties

The adsorption of organic materials by clays changes the surface of the surrounding medium, thereby affecting their interaction with water and electrolytes. The formation of interparticle bonds will also modify aggregates' swelling properties and strength since the possibility of positional adjustment is restricted (Greenland, 1965b). The significance of the location of an organic molecule within a soil aggregate has received as yet relatively little attention. However, it may be very important to determine the extent to which the clay-organic interaction modifies the soil's physicochemical, physical, and biological properties. Quirk and Panabokke (1962) and Willimas (1965) have obtained evidence that natural organic materials lining relatively coarse pores (of the order 50 µ c.s.d) exert the most important effects on the strength of aggregates. Emerson (1959) presented a model of the structure of soil crumbs, in which he indicated that the organic polymers were excluded from the internal surfaces of clay domains. This is probably correct but accurate, but there is no satisfactory evidence to show what proportion of clay surfaces are covered by organic materials. Williams 91965) has shown that when an aggregate is placed in contact with a solution of a strongly adsorbed polymer such as polyvinyl alcohol, the polymer penetrates only the periphery of the aggregate. Thus, even in surface soils, there may be as many clay surfaces free of organic materials as there are surfaces on which organic matter is adsorbed. Some qualitative ideas regarding the effects of adsorbed organic materials on the properties of soils can be obtained from the changes that occur when organic compounds are added to clays and when organic materials are extracted from or destroyed in soils. Correlation between the amounts of total organic matter of components of the organic fraction and certain soil properties have been used to provide information regarding the effect of the organic materials (Greenland, 1965b).

Organic cations are less strongly hydrated than inorganic cations. Consequently, when inorganic cations are displaced from clay surfaces, the affinity of the clay for water is reduced (Hendricks, 1941; Greenland *et al.*, 1964). The decrease in the tendency of the clay to adsorb water is more pronounced with alkylamines containing more than six carbon atoms. This indicates that the effect is due not only to the lower hydration energy of the organic cation but also to the displacement of water from the clay surfaces by the hydrophobic alkyl groups. "Waterproofing" of clays by adsorption of alkylammonium compounds has been extensively studied about its potential use in stabilising soils for engineering

purposes (Clare, 1947; Chakravarti, 1956). A similar mechanism may account for the nonwetting of certain sandy soils. Such soils are fairly widespread, and their nonwetting seems to be because the sand grains are coated with hydrophobic organic materials (Thornton *et al.*, 1956; Bond, 1964). It has been found that complex formation enhances the sorption of various diamines from aqueous by montmorillonite in the presence of Cu and *vice versa*. The effects were measured quantitatively, and the resulting structures were investigated using X-ray diffraction. No direct correlation was observed between cell height and the configuration of the interlayer complex ions. "Keying" of organic and organo-metallic cations into the oxygen surfaces is inferred (Bodenheimer *et al.*, 1962).

The adsorption of certain organic compounds causes increased swelling in some clays. Thus, butyl-, propyl- and amyl-ammonium vermiculites may show extensive swelling in water (Garret and Walker, 1962). The effect is probably due to the formation of 'iceberg' or clathrate structures on the surface of the mineral. Partial displacement of calcium ions from montmorillonite by small alkylammonium ions also leads to extensive swelling, probably due to the disruption of water structures between the adjacent lamellae (Greenland et al., 1964). In both instances, the effect seems to be rather critically dependent on the surface density of charge of the mineral. When adsorbed, amino acids also induce increased swelling (Barshad, 1952; Greenland et al., 1962). This is due to the increase in the dielectric constant of the medium separating the lamellae. Where adsorption of an organic compound increases the tendency of the clay to swell in water, the residual inorganic cations should be more readily exchangeable. This has not been established, but it has been shown that displacement of small aminoacid cations from vermiculite or montmorillonite is difficult only when they cause a partial closure of the lamellae (Greenland et al., 1965). When alkylammonium ions that decrease clays' swelling are adsorbed, not all the inorganic cations can be displaced (Greenland and Quirk, 1962). The mechanism by which this restriction in the freedom of the inorganic cations occurs is not entirely clear. Hendricks' (1941) original concept of a steric covering of the inorganic ions, perhaps best supported by the data of Weiss (1959) has been widely accepted. For montmorillonite, the decreased interlamellar distances may also restrict movement. However, the adsorption of a layer of uncharged polyvinyl alcohol 10 A⁰ thick on all surfaces of sodium montmorillonite produced no decrease in the cation exchange capacity (Greenland, 1965b).

The non-humified organic materials in soils have a small external and large internal area, in common with other cellulosic materials. Thus, to obtain information about the effect of adsorbed organic compounds on the accessible surface of the clay, this material should first be removed. When this is done, the removal of the remainder of the organic matter leads to an increase in the specific surface area (Burford *et al.*, 1964; Mitchell *et al.*, 1964). Kuron *et al.* (1961) noted an increase in ethylene glycol adsorption after several soils' peroxidation. Aleksandrova and Nad (1958) reported that peroxidation of a clay-organic complex increased water adsorption. Thus, the organic materials must fill or block pores made available by their removal.

Green moss contained 11.44% and fresh oak leaves 5.44% (dry matter basis) of water-soluble organic matter containing about 52% C. The brown aqueous extract was absorbed on activated charcoal, which removed most of the colour, leaving an almost colourless solution. The absorbed fraction contained substances capable of being absorbed by soil minerals, producing organo-mineral complexes (Khan, 1951).

A study of the reaction of different clays with anaerobically fermented grass extracts found that montmorillonite and other high base-exchange clays favour the formation of a dark clay-organic complex. The clay should have a high exchange capacity for forming a dark clay-organic complex— Na clays sorb more organic matter, giving darker products than H, Ca or Mg clays. Organic complexes do not sorb at alkaline pH, but their sorption was appreciably high in acidic pH, suggesting that black cotton soils are formed in periodic anaerobic conditions. Sorption of organic matter and the formation of dark colour have always been associated with Fe, Mn, ca, and Mg, which may contribute to the dark colour of the clay-organic complex (Singh, 1956).

The physicochemical relationships of humic substances to mineral colloids and humus-clay complexes of the main soil types in Czechoslovakia have been discussed by Najmr (1963), along with the importance of organo-mineral colloids in soil fertility and in improving sandy soil. The humus-clay complex is characterized by the humic acid fixed to clay on the one hand and saturated with divalent or trivalent cations on the other. The amounts and the amounts and ration of these components are the characteristic features separating different genetic soil types.

The surface areas of soils were determined before and after the removal of organic matter by treatment with H_2O_2 . The external area, determined by low temperature N adsorption, increased after peroxidation. The total area derived from the N area and cetyl - pyridium bromide (CPB), adsorption generally decreased. Part of the clay-organic complex was separated from some soils, and this material's external and total surface areas before and after peroxidation were determined similarly. Both the external and total areas increased after peroxidation. Results indicate that soils contain organic materials that are not part of the clay-organic complex and that adsorb large amounts of CPB on surfaces not accessible to N molecules. Peat showed a correspondingly high CPB adsorption and low N area. The large differences in the N and CPB areas after peroxidation show the importance of removing organic matter before determining the surface areas of soil clays. The surface areas were only slightly greater when carbon was completely removed by 30% H_2O_2 than when it was partly removed by 6% H_2O_2 . Organic compounds associated with the clay in the clay-organic complex can prevent access of N molecules to many of the clay surfaces and probably exclude CPB from some of these surfaces (Burford *et al.*, 1964).

IR adsorption spectra of several carboxyl compounds adsorbed on bentonite-clay showed the expected carboxyl shifts and an even more constituent change in the relative intensities of the 'bonded' and 'free' hydroxyl peaks. This change in relative intensities may be a useful criterion for judging the importance of hydrogen bonding to the adsorption process (Lardon and Sherman, 1964). Wilk (1964)

studied the formation of humic compounds from 0.1M Na4P2O7 soluble humus complexes and clay minerals in the laboratory and inferred that there was no chemical bond between the humus complexes and crystal lattices of kaolinite and alkalinite, the humus complexes were mechanically adsorbed on the minerals.

Bentonite and, to a lesser degree, illite mainly adsorb the high-molecular-weight fraction of humic acid. Kaolinite adsorbs the fraction with a low degree of condensation. The sorption power increases in the order of kaolinite < illite < bentonite. Humic acids corresponding to substances originally adsorbed could be successfully extracted from complexes with bentonite and illite only after hydrolysis with $1N H_2SO_4$ or after treatment with HCl + HF (Flip, 1968).

On centrifuging a humic acid (extracted with NaOH) from black earth in Spain and eluted through Dowex 50-W with Na-saturated bentonite ($< 2 \mu$), the interlayer spacing of the clay was increased up to 30 A⁰. The d₀₀₁ spacing was increased by increasing the humic acid/clay ratio and with increasing shaking time (up to 8 hours), and decreased with an increase in pH of the humic acid solution (Martin and Perez, 1969).

Lower pH values indicated complex formation in AlCl₃ / humic acid systems in the initial part of the titration curves and by the disappearance of the buffer zone around pH five that corresponded to Al hydroxide formation in the AlCl₃ system. The complexes were formed readily in strongly acid conditions; they were transformed into hydroxy Al complexes above pH 5 and disappeared around pH 9 (Yoshida and Nakao, 1971). The nature of the valency bonds between humic and clay fractions on lateral surfaces of the octahedra layer was established by determining the ion exchange positions on basal and lateral surfaces of clay structures before and after digestion with H₂O₂. The bonding was found to be the result of the change resulting from the breakdown of the octahedral layer by the strong acid system in the soil absorption complex (Ganev, 1972).

Reactions between humic acid and clay minerals were studied in fresh water and in 3.5% sodium chloride solutions. In freshwater conditions, clay minerals (chlorite, illite, kaolinite, and natural sediments) with sizes less tha 4 μ diameter can adsorb less than 0.4% of the humic acid. In contrast, those clays can adsorb more than 2.5% in NaCl solution. Increasing the acidity of the reaction media causes enhanced adsorption. The order of increasing adsorption capacity of the clay minerals in simulated sea water conditions (3.5 % NaCl at pH 8.1) is chlorite > illite > kaolinite. Experimental adsorption processes are almost completely reversible with changes in the electrolyte strength. X-ray diffraction studies of the organo-clay complexes indicate that the organic matter does not alter the structures of the clay minerals. Infrared and thermogravimetric analyses suggest that the carboxyl groups of the humic acid participate in chemical bonding with the clay minerals. The results of these studies indicate that short-term exposures of clay minerals to humic acids yield mainly physically bound organo-clay complexes. At the same time, some chemisorbed bonding takes place through carboxyl groups. An electrochemical model is proposed that depicts the relative importance of coulombic and

van der Waal's forces in the adsorption processes of humic acid on clay minerals in varying chemical environments (Rashid et al.,1972).

Ca formed two types of complexes with humic acid and fulvic acids: a pseudo-soluble complex where Ca was bound only to COOH groups and a flocculated form here Ca was fixed on both COOH and OH sites. The stability of these complexes was studied in exchange reactions with monovalent ions, and changes in the structure being monitored by differential thermal analysis (Dupis and Jambu 1973).

The electron micrographs (from black chernozem) of illite and smectite indicate that the material has a smectite base with a fine granular surface. The granules seemed to form an integral part of the complex. Dormaar (1974) found that the scanning electron microscope proved to be suited to show the physical associations of organic and mineral matter from a black chernozem Ah horizon.

The presence of complexed and non-complexed amorphous Fe and Al were used to distinguish cambic and spodic horizons. Intergrade profiles were similarly divided into Inceptisols and spodosol (Bruckert 1975). The role of exchangeable cations in forming clay-humic complexes and quantifying the effect of organic matter on a given physical, physico-chemical clay property are studied through model analysis (Chass in 1976).

HA complex formation and intermicellar adsorption by 2:1 layer type of clays were investigated by IR spectra and X-ray diffraction analysis after incubation of bentonite with pink bark or rye straw and after shaking HA extracted from Eustis soil with bentonite. Molecular weight separation by Sephadex G50 and G25 gel filtration of the humic compounds indicated a composition compound of molecular weight fractions in the range of 1000-30,000. The humic fraction with a molecular weight of 1000-50,000 appeared to be the most active in complex formation. IR analysis revealed that after treatment with organic matter, bentonite had spectrograms exhibiting bands at 1440 and 1400 cm-1 for COO⁻ vibrations, indicative of an interaction between HA and bentonite. Only surface reactions were observed and intermicellar adsorption of humic compounds could not be substantiated by X-ray diffraction analysis as was obtained using ethylene glycol (molecular weight 62), which expanded the bentonite d001 spacing from 12.4 - 17.0 Å. The absence of a shift to higher spacings indicated that the humic fractions could not penetrate the intermicellar regions. Molecular weight and molecular volume determinations of humic fractions showed radii exceeding the expansion limits of interlamellar spaces of bentonite. The effect of cation saturation of clay in aiding interlamellar adsorption of humic compounds was also found to be of no significance. A mechanism was proposed for interlamellar adsorption of humic acid based on marginal curling of clay surfaces due to attack by weathering processes (Tan and Mcgreery, 1976).

The nature and strength of the bond of humus and its components with minerals and the bond of the organic matter molecules with each other and with cations were discussed by Gorbunov and Orlov (1977). The authors found that random, non-oriented penetration of humic acid is possible only if the humic acid molecule is flat and about 5-8 Å (average diameter of humic acid is 70 Å) thick. The absorption of humic acid was observed to follow the equation Y = axb where Y = amount of humic acid

adsorbed by the mineral (% of the sample), x = equilibrium concentration of humic acid in solution (mg/ml) and a (0.05-0.5) and b (0.3-1.0) are constants. This equation made it possible to estimate quantitatively the interaction of humic acid with the mineral components of soils and rocks that leads to the aggregation of soils and to an increase in the stability of humus, which is important under extreme irrigated soil conditions (flooding) or for storing a humus layer.

The CEC of lowland peat humic acids was dependent on both the degree of polymerization of humic substances and the change and polymerization properties of the cations. No AEC was apparent. The rodex capacity was high due to the presence of a semiquinone-type nucleus. The interaction between humic acids and metal ions involves physical adsorption and chemical ionic or chelate bonds (Meisel et al. 1977).

The nature of the binding of divalent metal ions by humic acid was examined by a modified potentiometric titration procedure involving sequential addition of metal ions to solutions of the humic acid of constant pH. At pH values below the point of oxide hydrate formation, the drop in pH resulted from the release of protons from participating reactive groups; at higher pH values and at high M2+/HA ratios,

additional protons were released from the hydration water of the metal held in 1:1 complex. At least two major sites were involved in the complex formation. Stability constants were in excellent agreement with those obtained by conventional titration and followed the order Cu > Pb >> Cd > Zn. Differences between humic acids in their ability to bind divalent metal ions were negligible (Stevenson 1977).

The importance of the preparation mode on the hydration properties of montmorillonite - humic acid association were shown, and some results of nitrogen adsorption by these complexes were presented by Chassin et al. (1978).

Localization of the OM in the pores of the clay plays an important role; this localization depends on the mode of preparation and carbon content. A general interpretation of the action of OM on the hydration properties of these associations was also given.

The response of rice yields to mixed cropping of vetch-rye grass used as green manure was better than with vetch alone. Incubation tests with the addition of 2% OM to soil showed that the degree of formation of organo-mineral complexes was greater with rye grass than with vetch (Vicia sativa). Humic substances from the former were more firmly combined with the clay than with the latter. The increase in viscosity, ammonium absorbing capacity, and buffer capacity of organo-mineral colloidal complexes helped to promote the aggregation of the soil and increased its retaining power for plant nutrients (Fu and Chang 1978).

The behaviour of ferric EDTA and ferric citrate in nutrient solution and their interaction with humic acid was investigated at pH levels of 5-7 using the technique of membrane ultrafiltration to separate small iron species from high molecular weight products of hydrolysis and to estimate the binding of iron by humic acid. Ferric EDTA was found to be of small molecular size at all pH values,

whilst ferric citrate solutions contained an increasing proportion of high molecular weight material as pH was increased. Some iron present in both solutions was bound by humic acid at all pH values. Studies were also conducted on the uptake of iron by wheat roots from nutrient solutions containing either ferric EDTA or ferric citrate and the effect of humic acid on uptake. At all pH values, more iron was absorbed from ferric EDTA than from ferric citrate. Increasing pH resulted in a progressive decrease in iron uptake in both cases. The presence of humic acid depressed iron uptake at all pH values (Linehan 1978).

A series of synthetic amorphous aluminosilicates, hydrous oxides and allophanic soil clays were treated with aqueous extracts of humified clover. The resulting changes in surface charge were determined by comparing the charge characteristics of these organic-treated samples and those treated with a synthetic mixture of the inorganic components of the humified clover extract. Organic treatment caused a change in net surface charge to more negative values. The charge varied with the mole ratio Al/Al+Si of the alumino-silicate, being largest at low ratios. Where the alumino-silicates contain positive charges, these are reduced by the organic treatment. This is a major contributor to the alteration in net surface charge in more aluminous samples. The effect of organic treatment on the charge characteristics of allophanic soil clays was similar to that for the synthetic aluminosilicates of intermediate composition. The inorganic treatments also caused an increase in negative charge, and this is attributed to the neutralization of positive charge balancing Al-hydroxy material. These effects are discussed regarding the degree of polymerization of charge-balancing hydroxy- Al (Perrott 1978a). Freshly formed water-soluble OM extracted from humified clover leaves was used to treat a range of amorphous aluminosilicates and hydrous alumina. Phosphate retention isotherms were determined on the resulting organo-mineral complexes. The organic treatment reduced phosphate retention by hydrous alumina and amorphous synthetic aluminosilicates with high and low Al/Al+Si mole ratios. There was no depression of phosphate retention with amorphous aluminosilicates of intermediate composition. Similarly, organic treatment did not reduce the phosphate retention capacity of an allophonic soil clay of intermediate mole ratio. These results appear to be due to the degree of polymerization of chargebalancing hydroxy-Al in the aluminosilicates (Perrott 1978b).

The molecular weight (mwt) and molecular weight distributions of humic substances and metal humates of different origins have been determined as a function of pH and electrolyte concentrations by analytical ultracentrifugation and gel filtration methods. Average mwt and particle size point to low pH molecular aggregates in an aqueous solution. These aggregates rapidly decompose at higher pH. The change in molecular weight of humic acids of various origins and ages and their behaviour as a function of pH support the fact that in addition to the age of the sample, all conditions prevailing during the complex transformation must be taken into consideration in the interpretation of the colloidal structure. Trivalent metal ions almost exponentially increase the molecular weight of humic acids, while divalent cations cause only a linear increase. The effect of the magnesium ion is negligible, even at higher electrolyte concentrations. (Sipos et al. 1978).

From TG/DTG data, percentage weight loss and activation energy values,

 $E = -4.35 (Log B2-Log B1)/(T^{-1}) 2-T^{-1}(-1) 1)$

where B2 and B1denote the heating rates at 20°C/min and 10°C/min respectively have been determined. From the results of the thermal behaviour of the organo-clay complexes, it appears that when Na and Ca ions are saturating cations, the molar ratio of clay: HA/FA are higher than that for clay-organic complexes and the peak temperatures, so also E values. The variation of E value in the case of Na/Ca clay complexes with HA and FA is not so sharp as Na and Ca²⁺ ions have considerable influence on association- dissociation equilibria of clay-metal-organo-complexes. The nature of the bonding with clay-organic matter complex may not be the same as with metal-clay inorganic matter complexes (Adhikari et al. 1979). The alignment and orientation of organic molecules to clay surfaces (cf. edge and interlayer) are different, with different degrees of saturation. Hence, activation energy values for decomposition reaction differ from complex to complex, and no correlation could be drawn between the peak temperature and activation energies with molar ratios and with saturating cations of clays. Free sesquioxides coat the clay surface. As a result, the authors observed that the interaction was not strong. Still, after removing sesquioxides, more clay surfaces are exposed to interaction with organic molecules, resulting in more adsorption and strong covalent bonding between clays and organic molecules. Therefore, the peak temperatures and activation energies are shifted to the higher side.

In the surface soil layer, organo-metallic complexes are formed, which are important in biological processes. An attempt by Beskrovnyi et al. (1979) to synthesize complex-forming active compounds showed that thermal and radiation treatments of aqueous solutions of sugars, phenols and organic acids with pK higher than 1 in the presence of transitional metal ions, an oxidizing agent and a phosphate buffer resulted in the formation of biologically active compounds. Chemical and physicochemical investigations showed that these compounds consisted of metal-containing humus-like substances similar in many characteristics to weakly humified simple humic substances. These methods of "biologically active compound" formation and the reaction involved simulate (to some degree) various modes of humus formation in nature.

Houbenov et al. (1979) studied the interactions between monoionic montmorillonites, saturated with Na, Ca, Mg or Al, and ammonium humates and fulvates at pH values ranging from 4-8 resulted in the formation of organo-mineral complexes. They observed that with increasing additions of organic matter, a progressive expansion of the lattice of monoionic montmorillonites occurred; the expansion was less at higher pH values.

2. d) Naturally occurring clay-organic complexes

That humic materials absorb or be absorbed by clay particles was known to scientists, even in the early 19th century. Schloesing (1874) attempted to separate the humus from the clay by suspending the mixed sol in ammonia and then adding ammonium chloride, which flocculated the clay but left much of the humus in suspension. He also found that the quantity of chloride required to flocculate the clay

increased with the amount of humus present, a phenomenon that was first investigated by Fickendy (1906). The structure of the mixed clay-humus suspensions were investigated by several authors using different methods in the earlier part of this century. Thus, Myers (1937) used viscometric methods; Sideri (1936) used optical methods. They concluded that the adsorption of humus by the clay induces the formation of mixed clay-humus micelles in which most of the clay particles possess a fairly definite orientation. There was no evidence that the organic colloids ever entered into the crystal lattice of the inorganic colloids; in fact, Sedletsky and Tatarinova (1941) found that the electron diffraction pattern of the clay-humus complex only possessed the unaltered lines of the clay. However, when drying, the two colloids can form mixed micelles, which give mixed microaggregates of clay and humus. Tyulin (1938) developed a method for fractionating clay-humus complex and proposed a classification of this complex relating to soil fertility. Tyulin's method was utilized by Vinogradov (1942) and Atkinson and Turner (1944). In India, Ramamoorthy et al. (1957) also studied clay-organic complexes using Tyulin's technique, which some other workers modified. They used black cotton soil, infertile acid cinchona soil, composted FYM mixture with clay minerals, or freshly precipitated R203. The ratio of Group I/Group II colloidal complexes was 3.34 in fertile soil (as compared with 1.75-2.47 in chernozem) and 4.79 or very high with montmorillonite and SiO₂ mixture; it was 0.154 in the infertile soil (as compared with 0.59-0.77 in podzols) and 1.79 or considerably less with mixtures of kaolinite, A1203 and Fe203 respectively. Results suggest that montmorillonite and active sio2, tetrahedra on the surface of clay promote the formation of the fertile group of clay-humus complexes, and the presence of kaolinite and abundance of octahedral A1203 or Fe203 favour the infertile second and perhaps the third group.

By titrating soils that are moistened with water until they remain plastic, the "physical clays" are separated without imparting their composition or properties. It was in this way possible to localize the humus in the organo-mineral particles of the soil particles less than 0.01 mm in dia, and the amount of "physical clay," i.e., true mineral matter of less than 0.01 mm grain size, and the total humus in the organic-mineral matter could be determined. The saturation coefficient of the clay concerning humus, i.e., the amount of humus per unit of physical clay, varied between 0.05 and 2.00, and, together with the clay assay, indicates how well the soils will aggregate, and the agricultural usefulness of a soil (Godlin 1959).

Hashimoto and Harada (1959) found no significant differences between high-yielding and ordinary fields in the total amount of readily soluble humus accumulated on GL colloidal complexes. On high-yielding fields, FYM was effective. In the not-readily soluble humus, there were no significant differences between the content of brown and grey humic acids or between the proportion of grey humic acid to the sum of humic acids and the total amount of soluble humus. Humification is thought to be less rapid in high-yielding fields.

In mixtures of 3% humic acid with clay suspensions of different Ca saturation, there was a gradual decrease in the initial acidity of the humic acid (pH 4.56) to a stable level of pH 5.1-5.8 within 38 days; potentiometric titration of the mixture and its components indicated that this decrease in acidity was
due to the fixation of acidoid functions by the clay-humus complex. Fractionated flocculation showed that a much smaller concentration of KC1 (0.04-0.06 M) was required for flocculating the clay-humus complex than for flocculating the humic acid alone (0.6 M). About 20% of the dispersed solid phase, rich in humic acid, strongly resisted the action of the electrolyte (Eschena 1963).

Coarse, medium (0.2-0.14 μ) and fine clay fractions were separated from a solonetz Bt horizon by Arshad and Lowe (1966). Organic matter was extracted by successive treatments with 0.1M Na4P207 (pH 11), 0.1N NaOH, HF/HCl and finally Na4P207. The fractions and their mineral and organic components were characterized by C and N analysis, X-ray diffraction, IR and EM examination. The largest portion of complexed organic matter was associated with the coarse clay fraction, which contained relatively large amounts of kaolinite; only traces of kaolinite were found in the finest particles. The proportion of extractable OM increased with a decrease in clay-particle size. C/N ratios of extracted humic acids decreased, and the prominence of aliphatic structures increased with decreasing particle size. Aromatic structures in humic acids increased with growing resistance to extraction. There was no evidence of OM adsorption in the clay's interlamellar spaces.

The infrared spectra of fine fractions of the A horizon of a Cuban dark compact tropical soil suggest that the most probable bonds between organic compounds and clay minerals are H bonds with and without participation of H_20 and bonds involving amorphous R_20_3 (Stepanov 1970).

Clay-organic matter complexes ($<2 \mu$) separated from Leavitt loam (black chernozemic soil) by ultrasonic dispersion had essentially the same thermal decomposition properties as the organic matter separated from the same soil with alkali. The thermograms of the easily extracted materials had a high-temperature peak only when treated with acid. Still, those difficult-to-extract and coarser residual materials (silt and roots) had a high-temperature peak (Lutwick 1972).

After a preliminary ultrasonic treatment of samples of volcanic ash soil to disperse the aggregates, fractionation using sieving (2 mm - 53 μ), gravitation sedimentation (53 - 5 μ) and centrifugal sedimentation (<5 μ) gave reproducible results for the content of each fraction. Most of the plant debris were separated from organic matter of organo-mineral complexes, and the clay mineral content of the sand and silt fractions was low. Primary minerals were absent from the <0.5 μ fractions. Clay mineral and organic matter contents increased with increasing particle diameter of the fractions, but the C/N ratio and log K values (in the extracted humic acid) decreased. Over 50% of the organic matter in the samples receiving ultrasonic treatment was present in the <2 μ fractions. Ultrasonic treatment thus readily destroyed the linkage between primary minerals and soil organic matter or clay minerals with soil aggregates but did not destroy the linkage between clay minerals and soil organic matter (Satoh and Yamane 1972a). Samples of volcanic ash primarily subjected to particle size fractionation were further fractionated densimetrically using the bromoform-ethanol systems. Silt and coarse clay (2 mm - 0.5 μ) contained almost all the densimetric fractions. The organic matter and crystalline clay contents in these fractions increased with decreasing fraction density. Organo-mineral complexes in the silt fractions showed a predominance of amorphous matter and iron oxides. Complete separation of the organo-

mineral complexes was not attained because flocculation of the particles occurred in the heavy liquids used (Satoh and Yamane 1972b).

Inoue (1973), in a preliminary study of organo-mineral complexes in a glassy volcanic ash soil containing imogolite and allophane as principal clay minerals, indicated that as much as 18% of the humus was present as a stable organo-mineral complex. X-ray diffraction data and IR spectra suggested that the humus was complexed by surface bonding rather than incorporated into the imogolite structure. Aleksandrova et al. (1974) reported that heteropolar and complex heteropolar salts and sorbed complexes are the main components of organo-mineral colloids. Experiments with ascarite and humus from various sources showed that humic compounds did not penetrate the inter-layers of the mineral. Humic compounds persist in the form of clay-humus complexes.

Ultrasonic treatment was applied to the residue of the conventional alkali-pyrophosphate extractable humic acid A fraction in water to give a clay-associated HA-B fraction. This procedure yielded 60-67% of the humus of chernozemic and luvisolic soils. The HA-B fraction behaved in tests as a weakly humified, potentially labile component stabilized by adsorption to clay. The extinction coefficient at 280 nm (E280) of low ash humic acids was positively correlated with C: H ratio and negatively correlated with percentages of hydrolysable C and N. The E4/E6 ratio increased with decreasing molecular weight (Anderson et al. 1974).

Fractions of andosol aggregates separated chemically and by density were examined by transmission and scanning electron microscopy. Two layers of amorphous organo-mineral complexes coating halloysite primary mineral and organic debris particles were distinguished. The first consisted of humic acids containing large amounts of Fe and Al; the second consisted of fulvic acids containing little metal (Hetier et al. 1974).

Fractions of various sizes were obtained from a soil sample after dispersion of ultrasonic vibration. Organo-clay complexes were further separated into six densimetric fractions by centrifugation in heavy liquids with the aid of surfactant and ultrasonic vibration to obtain dispersion. The light fractions (<2.25 SG) contained the largest proportions of organic carbon. Some mineralogical differences were found, particularly a concentration of Fe and Ti minerals in the heavy fraction (>2.60 SG) and Ca-, Mn-, and P-bearing materials in the light fractions. Difficulty removing surfactant absorbed by the complexes was the main problem encountered in the method (Turchenek and Oades 1974).

Data for four paddy soils showed that organic C contents tended to be higher and that C/N ratios tended to be narrower organo-mineral complexes involving the finer mineral particles (Yonebayashi et al. 1974).

The extent of protonation of organic bases in clay-water systems depends on the adsorptive properties of the organo-clay species involved, as well as the structure and degree of hydration of the clay system. Organic molecules that disperse cationic charge over two or more condensed aromatic rings give rise to greater surface-induced protonation than single-ring organic molecules with similar solution pKa. Protonation in clay suspensions is frequently far more than that predicted based on electrolytic suspension pH and solution pKa of the organic base. For a given organic base, protonation in a clay film exceeds that in the suspended clay system. Protonation in an organo-clay film increases as the film moisture content decreases. The extent of protonation in organo-clay systems varies with cation species, cation saturation, and clay type (Karickhoff and Bailey 1976).

Inorganic-organic associations are especially important in tropical soils of volcanic origin on several islands in the West Indies. These soils tend to accumulate large amounts of OM, which is extremely stable but appears to be associated with their infertility. After examining most of the available information on the subject, it was concluded by Griffith and Schnitzer (1976) that the excessive stability or low turnover rate of the OM in these soils arose from it being strongly complexed by relatively large amounts of amorphous inorganics and that the formation of metal-organic complexes of such a nature interfered with the biodynamics of these systems. Their work aimed to describe the extraction and sequential purification of metal-organic complexes from these soils and present data on several analytical characteristics of the complexes at different stages of purification as revealed by chemical, spectrophoto- metric and thermal methods. The soil samples were collected on the Caribbean Island of Dominica.

During humification in an Atlantic climate, three main organo-mineral complexes are formed; humus-CaCO₃ in rendzina soils, humus-allophane in andosols, and humus-iron in brown acid soils. These complexes differ in their biological (ability to withstand biodegradation) and chemical (stability to extractants) properties. The humus-swelling clay complex, occurring in fluctuating pedoclimates, shows a high degree of polymerization of the organic matter (maturation). The temperate-humus forms are classified about the kind and degree of transformation of the fresh organic matter into:

--little-transformed humus (e.g. calcic mull and moder);

--strongly-transformed humified humus (e.g., acid mull, andosol);

--Very highly transformed, mature humus type (e.g., Vertisol, chernozem) (Duchaufour 1976).

A clay-organic complex was found in black Andalusian earth, which can be easily distinguished from montmorillonite complexes. The C/N ratio, however, is higher than in proteins. Comparisons have been made with montmorillonite complexes of amino sugars and t-disaminated proteins. The latter is similar to the natural clay organic complex from Andalusian black earth soils in chemical composition (Lagally et al. 1976).

Naturally occurring organo-mineral complex particles were separated from seven samples of volcanic ash soils (Satoh and Yamane 1972a) and were then divided into three types (blackish silt-sized, brownish silt-sized and clay-sized). The organic matter in the blackish complex fractions showed a higher exothermic reaction at about 390-460°C, the clay complex fractions had a lower exothermic response at about 300°C, and the brownish complex fractions showed both reactions. These exothermic reactions were similar to those of humic substances combined with inorganic materials such as Al- and

Fe-ions. The soil samples from the A horizons showed lower and higher exothermic reactions, but those from the B horizons showed only the lower ones (Satoh 1976).

Protein complexes of smectites in soils are difficult to detect if the usual smectite tests show no peculiarities. Andalusian black earths are typical examples. However, investigating alkylammonium derivatives allows the detection of adhered macromolecules that might be protein-like. Investigation of artificial clay-protein complexes reveals different types of clay-protein interactions. Calcium smectites adsorb proteins mainly on the external surfaces, anchoring macromolecules in the interlayer spaces. Nasmectites give partial crystalline products in which the silicate layers are distributed in the protein matrix. The exchange of alkylammonium ions can be used as a tool for the detection of the protein. Suppose this is adsorbed on external surfaces (Ca-smectites). In that case, the increased layer separation during the cation exchange enables the macromolecules to slip between the layers, and the basal spacing of the alkylammonium derivatives is changed in characteristic ways. Alkylammonium ions reorganize the Na clay-protein complexes to regular structures. The proteins are not displaced completely from the silicate surfaces to enhance the basal spacing (Perez Rodriguez et al. 1977).

Ochric brown soils developed on a large area of Fe- chlorite/greywacke in the Vosges have a bright red ochre colour and a pronounced fluffy microstructure.

These two properties appear associated with the abundant formation of amorphous organo-ferric compounds, which result from the adsorption of fulvic acids on the surface of ferric hydroxides. The fulvic acids result from the mountain climate, and the ferric hydroxides come from the weathering of Fe chlorite. These characteristics of ochre brown soils are not specific to the spodic horizons of ochric podzolic soils (Boudot and Bruckert 1978).

Gessa et al. (1978a) studied the effect of organic matter on phosphate sorption by organo-mineral complexes. Phosphate adsorption by three soils (one andosol and two brown soils) with different clay mineral compositions was studied. After treatment with H_2O_2 , each showed an increase in adsorption maxima values (x'm and x"m), and the andosol and a brown soil containing a vermiculite-chlorite intergrade showed the largest increase. Treatment with H_2O_2 did not modify the x'm/x"m ratio in the andosol. Still, this ratio was considerably lower in a "chloritized" brown soil, indicating a greater release of soils having less binding energy. After treatment with humic acid, the amount of phosphate adsorbed by the three soils differed; this could be attributed to the interaction between humic acid and the clay fraction.

In 24 soils, the CEC of untreated samples, samples treated with H_2O_2 and those treated with dimethyl sulphate was determined at pH 3, 5 and 8. The CEC and OM were calculated from multiple regression equations and compared with values after peroxide and methylation treatment. At pH 3 and 5, the CECs of clay by the three methods were similar, whereas at pH 8 they were significantly lower on untreated samples. The results are interpreted as the formation of organo-mineral complexes and to the interaction of the acid functions of the clay and OM (Gessa et al. 1978).

The lowest pH-dependent charge determined on untreated samples shows that the clay exchange sites in the organo-mineral complexes are those active between pH 5 and 8. In the soil, the mineral structures that can give negative charges in this pH range could be the non-crystalline Al and Fe hydroxides on the clay surfaces. Between these structures and the large organic molecules, strong bonds might stabilise the organo-mineral complexes and the lower pH-dependent charge of clay (and perhaps organic matter). This agrees with the interaction mechanism suggested by Greenland (1971). Such a mechanism, although not yet sufficiently tested, indicates the formation of oxygen bridges between the organic radicals and the Al and Fe atoms arranged in polymeric structures where coordinated water molecules are also present. Such a model explains why the pH-dependent charge of methylated samples does not differ from that of samples where organic matter has been removed.

The organo-mineral fractions of seven New Zealand top soils, members of a "climosequence", were isolated by ultrasonic dispersion in water and separated into sand, silt, and clay-size fractions. Several soils contained stable aggregates of mainly silt-size, cemented clay-size particles. The tendency of one soil (Mckerrow) to form larger aggregates by sand size was explained by its distinctive mineralogy. Total organic carbon and total nitrogen were used to indicate the amounts of OM in the organo-mineral fractions. In the sand-size fractions, the climate, and especially annual precipitation, strongly affected the quantities of OM, whereas, in the clay and silt-size fractions, the OM composition was affected (Tate and Churchman 1978).

Water-dispersible particles from six epipedons and one Bh horizon representing six different soil orders were separated into sand, silt and clay particles, and the clay-organic complex particles were further fractionated by density; organic C and N concentrations were lowest in sand; intermediate in silt, and highest in clay, but exceptions to this trend were observed and accounted for. Light clay-size, organo-mineral particles had

(i) high level of sorbed organic C;

(ii) wide C/N ratios; and

(iii) low amounts of alkali extractable C.

The reverse was true for heavy clay-size particles. A continuum of particle compositions existed between the density extremes, which differed for different soils. Their position within the soil fabric can explain the heterogeneity of clay-size particles. Light particles evolve at the surfaces by (micro-) aggregates and are exposed to the soil biosphere, whereas heavy particles occupy interaggregate space shielded from the soil biosphere (Young and Spycher 1979).

Organo-mineral complexes were separated from brown soils and chernozems. These were then chemically extracted to define the organo-metal and organo-mineral (clay) compounds. Brown soils consisted of loose aggregates characterized by a high content of organo-metal compounds consisting of fulvic acids with a high turnover rate. Chernozems, however, consisted of compact aggregates containing a high proportion of polycondensed humic acids and organo-mineral (clay) compounds resistant to microbial decomposition (Bruckert and Kilbertus 1980).

Schnitzer and Kodama (1967) have shown that organic substances of the fulvic acid fractionation separated from a podzol soil could penetrate the interlamellar region of montmorillonite. However, the natural occurrence of such a complex has not yet been observed (Greenland 1965a). The clay-organic complex was separated from A horizon of an acidic volcanic ash soil and studied by (Satoh and Yamane 1971) using the X-ray diffraction methods. The basal spacing of montmorillonite in the complex did not contract under the conditions that could contract the basal spacing of Na montmorillonite or that of the complex treated with H₂O₂. Various experiments suggested organic substances existed in the intermicellar region of montmorillonite in the complex separated.

In a study of orthic black chernozem in Alberta (Dudas and Pawluk 1968) slight differences in the morphological properties of Ah horizon were noted for soil samples at various locations within the black soil zone. It was felt that the morphological differences were largely due to variations in the degree of clay-organic complexes. The analytical data and electron microscopic observations (Dudas and Pawluk 1969/1970) indicate that the greatest organo-clay complexing from the three size fractions used occurs in the 0.2-0.08 μ fractions. Although larger amounts of organic matter occur in 2-1 μ fraction, the majority exists as free to uncomplexed organic matter. The data also suggest that the organic material is absorbed to the surfaces and edges of clay minerals and that clay hydroxyl groups contribute to the adsorption process.

3. Materials And Methods

3.1. Materials

Soil samples were collected from different parts of the country. Fourteen samples were selected for the present study based on the organic matter content and the clay content. The general description of the soils taken for the present study has been given in table 1. The air-dried soils were sonified with distilled Water, keeping the ratio of soil:water = 1: 2. The samples were given 4 mts treatment each time and were poured in 1 litre measuring cylinder. The $<2 \mu$ fraction of the clay-organic complex was siphoned out following Stoke's law till the upper 10 cm was clear. The collection of complex (the material for study) was continued the same way until the whole soil sample ceased to yield any material, i.e. the complex of $<2 \mu$ size. In general, 100 g of soil requires 29 minutes of treatment, except in Mohitnagar soil, for completely separating the clay- organic complex. Due to its low recovery, 34 minutes of sonification was found essential for the Mohitnagar soil.

To separate naturally-occurring clay-organic complex of $2-0.05\mu$ particle size, the suspension was kept for 2 months without disturbance and addition of any flocculating reagent. After that, the portion that settled below 30 cm depth was taken, giving particle size between 2 and 0.05 μ . The material remaining in the suspension above was filtered using a Sartorius membrane filter; thus, the <0.05 μ finer fraction of the complex was separated.

METHODS

The soil samples were dried, ground and sieved through a 2 mm sieve and stored for laboratory analysis.

Laboratory analysis

I. Studies with soils

i) To screen the existing methods for extracting inorganic amorphous constituents, the methods given by Hashimoto and Jackson (1960). Follett et al. (1965) (with hot and cold 5% Na₂CO₃) and Fey and Roux (1975) (using acid-ammonium oxalate, pH 3, solution) were compared using soils and clays.

Sl. No.	Soil		Parent material	Soil order	Clima	tic zone	Organic matter %	Clay content %	
	Place of collection	State	-		MAR mm	MAT ⁰ C			
1.	Bentlu	Himachal Pradesh	Old colluvium (Hill wash deposits)	Entisols	2100	26	2.41	20.00	
2.	Mohitnagar	West Bengal	Teesta alluvium	Entisols	2262	18	5.00	9.30	
3.	Karnal	Haryana	Alluvium	Entisols	721	26	1.26	18.30	
4.	Katwa	West Bengal	Alluvium	Entisols	1392	26	0.80	11.90	
5.	Jorhat	Assam	Brahmaputra alluvium	Entisols	1821	24	0.95	8.50	
6.	Henningkon glwa	Nagaland	Granite-gneiss	Alfisols	1900	23	2.64	22.30	
7.	Palampur	Himachal Pradesh	Glacial till derived from mixed rock type	Alfisols	3000	20	4.14	27.34	
8.	Naddi	Himachal Pradesh	Shale phyllites, slate	Alfisols	4000	17	1.72	14.00	
9.	Chikballapur	Karnataka	Granite-gneiss	Alfisols	790	23	2.41	23.75	
10.	Indore	Madhya Pradesh	Deccan Trap	Vertisols	929	24	1.26	54.00	
11.	Nandyal	Andhra Pradesh	Shales	Vertisols	765	27	1.03	55.00	
12.	Siraguppa	Karnataka	Granite	Vertisols	632	27	1.66	49.00	
13.	Kohima	Nagaland	Granite-gneiss	Ultisols	1920	24	4.02	12.20	
14.	Tamanda	Odisha	Alluvium	Ultisols	1557	28	1.95	9.30	

Table 1. Some basic information of the soils

ii) pH was measured by a glass electrode pH meter after equilibrating the 1:2.5 soil: Water and soil: *N* KCl suspension for 30 minutes (Jackson 1973).

iii) Organic carbon: This was determined using the Fe-0-phenanthroline indicator (Jackson 1973).

iv) Ca-CEC: This was determined by the method described by Jackson (1973).

v) Free iron oxides: Free Fe_2O_3 was estimated in the citrate-bicarbonate-dithionite extract (Mehra and Jackson 1960) colorimetrically using the method described by Krishna Murthy et al. (1970).

vi) Organic matter from the soils was extracted using 0.1M Na- pyrophosphate + 0.1M NaOH at pH 13 with a soil: extractant 1:10. The soils were kept in the extractant for 24 hours. The humic acid from the extracted organic matter was separated using Schnitzer's (1977) procedure. With the extracted humic acid, the following studies were conducted :

^o Carbon: This was determined using the Fe-phenanthroline indicator described by Jackson (1973).

^o Total N: This was determined by the Kjeldahl method (Jackson 1973).

° Optical density and E_4/E_6 ratio: These two parameters were obtained by taking readings in an alkaline solution of humic acid in a Hitachi (124) /1908 spectrophotometer at 465 nm and 665 nm wavelengths (Schnitzer 1977).

^o Infrared studies for functional group analysis: The 0.5 mg portion of humic acid samples dried P_2O_5 with 2 over in vacuum were mixed g KBr (IR grade) and 10 mg of this mixture was ground again with 190 mg of KBr. With this, a 200 mg (with approx. 0.0025 mg sample) pellet was prepared and run in a Shimadzu recording IR spectrophotometer (Type IR 27G) at a scanning speed of 10 minutes from 4000 to 400 cm⁻¹. The standard values of infrared absorption bands of humic acid are given in Table 2.

II. Collection of naturally occurring clay-organic complex

The soil samples in distilled Water (soil: water = 1: 2) were subjected to ultrasonic vibration using a SONI PROBE (Type 1180 A DAWE Instruments Ltd.) with solid titanium step horn (1/2) dia)

Minerals						W	ave No.	(cm ⁻¹)								
Kaolinite	3695	3670	3650	3620			1108	1038	1012	940	915	700		540		472
Halloysites	3695			3620	3400*	1640**	1108	1038	1020	-	918	695		545		474
Montmorillonite				3620	3400*	1604**	1100	1040	1020		915			520		470
Nontronite				3560	3400*	1640**	1130	1050	-		827			490		430
Muscovite				3628			1120		1020		928	828	750	535	480	
Biotite			3658	3550	-		-	1000				760	69	465		445
Vermiculite				3550	3380	1640		1	985			812	670		480	
Al- rich Chlorite			3620	3520	3340			1004		940		825	692	528		475
Gibbsite			3610	3525	3445	3395	1102	1030	975			800	745	670	560	540
Quartz				-			1172	1084				800	780	697	512	462
Microcline			-				1110	1030	1000				769	727	647	
Humic acid				-	3400	1700	1200	1050								
					2910	1630	1150									
					2845	1510										
		-	-			1450										
						1400										

Table 2. Infrared absorption bands of some soil minerals and humic acid

*Oh-stretching frequency for water molecules; **OH-bending frequency for water molecules

containing output power density at tip 500 W/inch², giving a frequency of 20 KC, pulsed at 100 cps with the overall dimension of the probe 14" long x $2^{3/4}$ " dia. The method is essentially what was described by Watson (1971).

A portion of the coarser fraction of the clay-organic complex collected after sonifying the soils were treated with 30% H₂O₂ to remove organic matter (termed as peroxide-treated complex in subsequent discussion). Another portion was given 30% H₂O₂ citrate-bicarbonate-dithionite (CBD) treatment and ammonium oxalate (pH 3) treatment in succession (termed as peroxide-oxalate treated complex). The following analyses were conducted in the laboratory, taking the natural, peroxide-treated, peroxide-oxalate-treated complex.

A. Physical Analysis

Surface area: Total surface area was determined following the method described by Carter et al. (1965)

B. Chemical Analysis

a) Organic carbon: This was estimated using the method described by Jackson (1973), which uses the Fe-orthophenan throline indicator.

b) Total N: This was determined by the Kjeldahl method (Jackson 1973).

c) Total elemental analysis :

 Na_2CO_3 fusion: SiO₂ was estimated gravimetrically from Na_2CO_3 fusion (Bear 1965). The melt was dissolved in 6N HCl and evaporated to near dryness. Dehydration of SiO₂ was obtained by HClO₄ treatment; finally, the acid was evaporated to fuming and the residue was backed on a sand bath. The residue was then dissolved in hot HCl, filtered, and washed free of Cl⁻. The filter paper and residue were ignited to constant weight and weighed as SiO₂,. The fusion extract after removal of silicon was analysed for the following elements :

Calcium and magnesium were determined by EDTA using calcon and EBT indicators (Jacks on 1973).

Potassium was determined with the help of a flame photometer (Jackson 1973).

Iron was determined colorimetrically using the procedure of Krishna Murthy et al. (1970).

Total sesquioxides were determined in the extract gravimetrically after precipitation by ammonium hydroxide (Jackson 1973).

Aluminium was estimated by subtracting iron content from the total R_2O_3 obtained from the above estimation (Jackson 1973).

C. <u>Physico-chemical Analysis</u>

a) Cation-exchange capacity: This was determined by the method described by Jackson (1973).
b) Potassium fixation: This was determined by taking
0.1-0.5 g sample (in suspension) and adding 1000 ppm K. Three alternate wetting and drying were
ensured before adding 20 ml water and subsequent centrifugation. K in the supernatant solution was

given unadsorbed K. Shaking with N NaOAc for 1 hr, and subsequent centrifugation gave exchangeable K. The total volume is always kept at 30 ml. The difference between total K added and unadsorbed K gave adsorbed K. The fixed K was calculated by taking the difference between adsorbed K and exchangeable K.

D. <u>Mineralogical analysis by X-ray of the complex after removing organic matter and</u> <u>amorphous constituents</u>

After removing organic matter, iron oxides, and amorphous constituents, the coarser fraction of the complex was analysed for qualitative mineralogy using X-ray diffraction. 200 mg of suspension was taken and saturated with Mg and K, and 10 ml of distilled water was taken to get a 2% suspension.

Parallel-oriented aggregate specimens of the sample were prepared on a glass slide (4.5 x 2.5 cm), taking 1 ml suspension in each case. Slides were dried at room temperature and then subjected to X-ray diffraction analysis.

Identification of clay minerals

Identifying each crystalline mineral species or series present in the sample is the purpose of the qualitative interpretation of a diffraction pattern (Jackson 1956). Since the diffraction pattern of each crystal species is a unique sequence diffraction maxima, like a fingerprint, the pattern serves to identify each species present. Ordinarily, dependence is placed on the most intense one to three diffraction peaks (from basal planes) for qualitative identification.

Several tables of diffraction spacings of crystalline substances are available (e.g. Brown 1961). The basal diffraction spacings of the layer silicates in soils, especially of the expanding lattice type, vary within limits, with the nature of interlayer cations and the salvation procedures employed. Thermal pretreatments are also necessary to distinguish some of the groups. As a routine, a minimum of five diffractograms are recorded with the following treatments:

(1) Mg-saturation; (2) Mg-saturation and glycerol solvation; (3) K-saturation;

(4) K-saturation and heating to 300°C; and (5) K-saturation and heating to 550°C. Special treatments (HCl dissolution, Na-citrate treatment etc.) may be required in Specific cases. The diagnostic criteria for the major clay mineral groups are summarised below:

(i) Kaolin group: Minerals in this group are characterised by strong reflections at 7.2 and 3.6 Å which disappear in heating the samples to 550°C. Thermal treatment also provides a means of distinguishing kaolinite from true chlorites. But many soil chlorites either get decomposed or lose the 7 Å peak when heated to 550°C or even at a lower temperature (Grim and Johns 1954; Rolfe 1954; Murray and Sayyab 1955). Identifying kaolinite under such circumstances may be based on chlorite dissolution by boiling the sample in HCl for a few minutes.

Halloysite of some soils gives a spacing of 10.1-10.7 Å, but more often, soil halloysite gives a spacing of about 7.6 Å on Mg-saturation and glycerol solvation. Heating to 400°C decreases the spacing to 7.2 Å (Brindley 1954).

Intersalation of kaolinite and halloysite with KOAc gives a 14 Å spacing (Wada 1961), and this can be decreased to a diagnostic 11.6 Å spacing on washing with 10N NH₄NO₃, Solution (Andrew et al. 1960).

(ii) Chlorite group: This group of minerals is identified by a series of basal reflections approximately at 14, 7, 4.7 and 3.6 Å, which persist on heating the specimen at 550°C. However, identifying iron-rich chlorites poses a problem, particularly in the presence of iron-rich 7 Å minerals. They have weak 001 and 003 reflections, with their strong 002 and 004 reflections overlapping the 001 and 002 kaolinite reflections. In clay chlorites, a series of defects are generally produced due to weathering, influencing the relative intensities of individual reflections (Bradley 1954). Defects in the structure may also cause partial expansion with glycerol (Stephen and MacEwans 1949), as found in the so-called" swelling-chlorites". This type of imperfect chlorites are identified by the 18 Å spacing in glycerol and 14 Å spacing on heating to 550°C. Chloritised montmorillonite/ vermiculite formed by fixation of iron and/or aluminium hydroxides in the interlayer space (Tamura 1956, 1958) under acid conditions of weathering is also common in Indian soils (Ghosh et al. 1962; Sehgal and Cornick 1971). The interlayer material from these minerals may be removed by treatment with either NH₄F or Nacitrate, or NaOH (Rich and Obenshain 1955; Tamura 1957). Before these treatments, these minerals give a 14 Å peak and do not collapse to 10 Å on K saturation and heating, but after the interlayer material has been removed, the resultant mineral either gives a 14 Å spacing (Rich 1960; Sawhney 1960) or an 18 Å spacing (Tamura 1957; Dixon and Jackson 1959) on glycerol solvation.

(iii) Micaceous minerals: This group of minerals is recognised by strong peaks at 10 Å and 3.3 Å on Mg-saturation and glycerol solvation. The dioctahedral illite also has a marked peak at 4.98 Å. The 10 Å peak is often asymmetrical in soil micaceous minerals with a tail extending towards a low angle. Such illites are termed "degrading illites" (Brown 1954) and are common in Indian soil clays. These degraded illites are now considered mixed-layer minerals. K-saturation often removes the asymmetry and produces a strong 10 Å peak in such minerals.

(iv) Vermiculite: Mg-saturated vermiculites on glycerol solvation give a 14. 2-14.4 Å peak. Kor NH₄-saturated vermiculites give a 10 Å spacing at room temperature or on heating to 300 °C depending on layer charge and/or interlayer islands of gibbsite or brucite. This mineral can, therefore, be distinguished from smectite by its non-expansibility on glycerol solvation and from chlorite by the collapsibility of the K-saturated sample on heating to 300°C. X-ray identification of vermiculites associated with smectite and chlorite poses an extremely difficult problem. True vermiculite gives only a low second-order peak at 7.0-7.1 Å and medium intensity peaks at 4.79 Å and 3.60 Å.

(v) Smectite group: The identification of smectite is based on the expansion of the Mg-saturated mineral to about 17.7 to 18 Å, on treatment with glycol and glycerol, respectively (MacEwan 1944, 1946; Walker 1958). Care should, however, be taken not to dry the sample at temperatures exceeding 35°C after saturation with Na/K ions and/or before glycerol or ethylene glycol solvation (Jackson et al. 1954). Montmorillonite has a fairly intense second-order peak at 8.9-9.1 Å. The spacing decreases on

K saturation and glycerol solvation, frequently giving a spacing of 14 Å. The peak shifts to 10 Å and is usually enhanced to give a sharp peak on heating to 300°C. Even after heating, a broad 10 Å peak indicates (Sawhney and Jackson 1958; Jackson 1963b) that the material has hydroxyl Al or sesquioxides interlayer material countering the layer charge and causing the mineral's thermal collapse resistance. Hydroxy Al or sesquioxide groups in montmorillonite and vermiculite provide clays and soils' inorganic pH-dependent cation exchange capacity (Jackson 1963a).

(vi) Attapulgite: It can be identified by a 10.2-10.5 Å reflection from the 110 planes, which is replaced by a broad halo on heating to above 400°C. A 040 spacing of 4.49 Å and a 440 spacing of 2.62 Å are also shown by attapulgite.

(vii) Interstratified or mixed-layer mineral group: There are two general types of interstratification possible: (a) a regular or ordered alteration of mineral layers in a definite sequence, for which the resulting superlattice spacing is additive of the basal spacings of the minerals present and their different orders (e,g. a 1:1 mica chlorite and 2:1 mica chlorite give respectively 24 Å and 34 Å peaks whereas a 1:1 mica-montmorillonite when glycerol solvated gives a peak at 27.8 Å), and (b) a completely random interstratification in which the layers do not repeat themselves in any regular sequence but are randomly distributed in the complex. A regular interstratification has a definite periodicity and may thus be considered to be more or less a well-defined crystal species than the random types. Random mixtures can be binary, ternary or quarternary interstratification involving two, three or four minerals. Binary random mixtures can be identified easily, but the higher types are difficult to locate (MacEwan et al., 1961).

The quantitative estimation of clay minerals in the sample was done according to Gjems (1967) with some modifications as Ghosh and Datta (1972) used.

(E) Infrared spectra of the complex with different treatments

Atoms grouped in molecules do not remain at rest but are continuously in vibration. Such vibration produces periodic atoms' displacements concerning one another, causing a simultaneous change in interatomic distances. The frequencies of the vibration fall within the range of 10¹³ to 10¹⁴ cycles per second, which is of the same order of magnitude. As the frequencies of infrared radiation, vibrations that are accompanied by a change in dipole moment give rise to the absorption of radiations in the infrared region of the electromagnetic spectrum. Several vibration modes may occur for a particular atomic group, each at a characteristic frequency and normally independent of other modes.

If molecules of a substance whose vibrations are accompanied by a change of a dipole moment are irradiated by a succession of monochromatic bands of infrared radiation, those radiated frequencies that correspond to the intramolecular vibrational frequencies may be absorbed wholly or in part. If a per cent of radiation absorbed by a substance is plotted against the incident wavelength (or frequency), the ensuing graph may be interpreted as intramolecular vibration. The graph, therefore, will be characteristic of the material and can be used in its identification. In addition, it should provide data on the structure and bonding and the characteristics within the molecule. For clay-mineral and organic matter (humic acid) studies, 2.5 to 25 μ wavelengths are used since the characteristic spectra occur in this range. Wavelength (λ) is conventionally expressed in terms of microns (μ) and frequencies in terms of wave numbers or reciprocal centimetres. The relationship is shown by :

$$1 \ \mu = 10^{-4} \text{ cm}$$

If $\lambda = 1\mu$, ----- $\frac{10^{-4}}{1 \text{ cm}^{-1}}$

 P_2O_5 dried 0.5 mg sample was weighed and mixed thoroughly with 2000 mg IR grade dried KBr. From this mixture, 10 mg was weighed and mixed thoroughly with another 190 mg KBr. The mixture was pressed (500 kg/cm² or 10 tons pressure) under vacuum for 15 mts to prepare KBr disc and was run in a Shimadzu recording IR Spectrophotometer (Type IR 27G) at a scanning speed of 10 minutes from 4000 to 400 cm⁻¹.

Infrared absorption bands for some selected soil minerals are given in Table 2. (F) Electron microscopic study of the complex with different treatments

(i) Basic techniques for grid preparation

The specimens to be examined in the electron microscope must be mounted on a thin supporting film to offer little opacity or scattering power to the electron beam. For a 60 KV beam, this attained at thicknesses of the order of 100 Å, However, a film of this thickness is fragile and requires support except in very small areas.

<u>Preparation of the supporting film</u> (Fig 1) :

The material used is polyvinyl chloride (Formvar).

(a) <u>Cleaning the water surface</u>

The following technique was used to cast the film on a water surface: (i) A deep glass bowl of about 20 cm diameter was used. It was filled up to 1 inch below its rim with distilled Water. Gross dust and traces of previous films (if fresh Water was not added) were swept off by putting a few drops of 3% (V/V) colloidion (nitro cellulose) in amyl acetate, allowing it to develop into a thin film. This film was swept off by using a strip of clean paper about 25 cm x 3 cm, which was smoothed into contact with the inside wall of the bowl, and about half of its width immersed. The ends were held by two pairs of tweezers or hands, which were then drawn round the wall of the bowl, pulling the paper loop across the surface behind them. The loop was closed, and the paper was withdrawn (1a). Amyl acetate vapours were again relied on to clean the water and used for many successive films. The bowl was kept covered when not in use.



Figure 1. Preparation of the supporting film

(b) Casting the film on a solid surface

A fresh mica sheet was cut into 8 cm x 3 cm size and cleaned with a needle in the middle of the layers . A left-hand angular cut was made on the top to indicate the clean surface facing up. The sheet was dipped in the film-forming solution for about 60-120 sec. It was withdrawn vertically, slightly inclined towards the inner side, and slowly enough to allow for draining and drying. The complete withdrawl was done in 90-120 sec. Drying was finally done in the open ir (in 50-55% humidity maintained by an automatic dehumidifier). After the film has dried up completely, the edges were trimmed off with a pair of scissors. The tough film was then made discontinuous towards the top with a sharp needle (1b).

(c) Floating the film on Water

The sheet was held on its sides between the thumb and fingers without touching the film. It was then stripped from the mica surface by floating it off on the water surface (1c).

(d) Mounting the film on grids

On the most uniformly thin region of a film cast on Water, 30-40, 3 mm discs of the 200-300 mesh grid, with rough surface down at roughly equal intervals, were placed. The fresh grids were used as such, while the previously used grids were first cleaned. (The used grids were dipped in chloroform for 15 min, to dissolve the old films. They were then washed in acetone by sonicating thrice for a total of 15 min. Acetone was changed after every sonification). Each grid was slightly depressed with a mounted needle to force the film into contact with the grid by a 2-3 min hydroplastic head. Whatman filter papers with 3-4 folds were brought nearer the grids lifted by the suction principle. The paper was lifted off as soon as it absorbed water. The film and the grids mounted are placed on a cleaned petri dish and allowed to dry in a desiccator.

(e) Sample mounting

The coarser $(2-0.05 \mu)$ as well as a few selected finer fractions $(<0.05 \mu)$ of the clay-organic complex with peroxide-treatment and peroxide-CBD-oxalate treatment were thoroughly sonified, and with each of these samples a 0.03% suspension was prepared. One drop of this suspension was mounted on a copper grid covered with Formvar film with the help of a platinum loop. The grids were examined in a Philips EM 300 Model electron microscope at an operating voltage of 80 KV.

4. RESULTS AND DISCUSSION

It is well known that crystalline components, humus, free oxides and allophones are involved in forming clay organic complexes in soil. In presenting the results of the present investigation, some of the soil properties have been given first, followed by the content and characteristics of the amorphous material and humic acid in the different soils. These results provide the basic information of the soils under investigation. In the next section i,e. (4d) nature and characteristics of the naturally occurring clay organic complex have been dealt with.

(a) Some properties of the soils

1. <u>pH</u>

The soil pH of 5 Entisols ranged between 5.5 and 8.1 (water) and 4.8 and 7.5 (N KCl). Among these soils, Jorhat and Bentlu had an acidic pH of 5.5 and 5.9; Mohitnagar registered a slightly acidic pH of 6.6, and Katwa gave 7.4, while Karnal had an alkaline pH of 8.1 in water (Table 3).

Among the 4 Alfisols studied, Palampur and Naddi had acidic pH values (in water) of 5.4 and 5.9, respectively, while Henningkonglwa was found to have slightly acidic to neutral pH of 6.7. The Chikballapur soil had an alkaline pH of 8.0 (water) (Table 3).

The three Vertisols had a pH range of 7.7 - 8.6 (water) and 6.3 - 7.5 (N KCl). The pH (water) values were 7.7, 8.1 and 8.6 for Indore, Siraguppa and Nandyal, respectively.

Kohima and Tamanda (Ultisols) gave acidic soil pH (water) of 5.5 and 5.0, respectively.

2. Organic matter content

The organic matter in the Entisols varied from 0.80 to 5.00%, with the maximum value associated with Mohitnagar soil and the minimum with Katwa soil. The values in Bentlu, Karnal and Jorhat were 2.41, 1.26 and 1.95% respectively (Table 3).

In Alfisols, the values ranged from 1.72 - 4.14%, with the minimum value observed in Naddi and the maximum in Palampur soil. Similar observations were made by Ghabru (1977) while studying soils from Himachal Pradesh. The Henningkonglwa and Chikballapur soils contained 2.64 and 2.41% of organic matter.

Sl. No.	Soils	p	H (1:2.5)	Organic	Ca-CEC	Free iron
		Water	N KCl	matter	me/100 me	oxides
				(%)		%
1.	Bentlu	5.9	5.1	2.41	23.12	3.36
2.	Mohitnagar	6.6	5.9	5.00	25.00	1.14
3.	Karnal	8.1	7.5	1.26	28.22	1.43
4.	Katwa	7.4	6.5	0.80	25.50	1.43
5.	Jorhat	5.5	4.8	1.95	14.75	1.54
6.	Henningkonglwa	6.7	6.4	2.64	14.25	3.40
7.	Palampur	5.4	4.6	4.14	14.37	3.14
8.	Naddi	5.9	5.3	1.72	21.25	2.86
9.	Chikballapur	8.0	6.8	2.41	19.06	4.42
10.	Indore	7.7	6.3	1.23	75.00	1.78
11.	Nandyal	8.6	7.4	1.03	61.87	2.50
12.	Siraguppa	8.1	7.5	1.66	75.75	0.89
13.	Kohima	5.5	4.7	4.02	20.62	3.93
14.	Tamanda	5.0	4.4	1.95	18.50	3.07

Table 3. Some properties of soils

The three Vertisols from Indore, Nandyal and Siraquppa were found to have 1.26, 1.03 and 1.66% of organic matter content, respectively.

Among the two Ultisols, Kohima had higher (4.02%) values of organic matter content than Tamanda (1.95%) soil.

3. Ca-CEC (me/100g)

The Entisols had the cation exchange capacity of 23.12, 25.00, 28. 22, 25.50 and 14.75 me/100 g in Bentlu, Mohitnagar, Karnal, Katwa and Jorhat soils (Table 3).

Among the Alfisols, Naddi had relatively higher values of 21. 25 me/100 g. The values for Henningkonglwa, Palampur and Chikballapur were 14.25, 14.37, and 19.06 me/100 g, respectively. Similar values were reported by Ghabru (1977).

The CEC values of the three Vertisols were maximum when Compared with other soils. The values were 75.00 (Indore), 61.87 (Nandyal) and 75.75 (Siraguppa) me/100g.

Table 3 shows the values for Kohima and Tamanda (Ultisols). The CEC values were 20.62 and 18.50 me/100 g.

4. Free iron oxides

Table 3 shows the values of free iron Oxides in soils. Among five Entisols, Bentlu gave a maximum value of 3.36%, while Mohitnagar had a minimum (1.14%) free iron oxide content. The values were the same (1.43%) for the Karnal and Katwa soils. Jorhat contained 1.54% of free iron oxides.

In Alfisols, the free iron oxide values ranged from a maximum of 4.42% in Chikballapur soil to a minimum of 2.86% in Naddi soil. The corresponding values in Henningkonglwa and Palampur soils were 3.40% and 3.14%, respectively. Among the three Vertisols, Nandyal had a maximum free iron oxide content of 2.50%. Indore and Siraguppa soils were 1.78 and 0.89%, respectively.

The Kohima and Tamanda (Ultisols) had a free iron oxide content of 3.93 and 3.07%, respectively.

(b) <u>Screening of the existing methods for extracting inorganic amorphous</u> <u>constituents</u>

For some time, it has been customary to determine soluble silica in soils and minerals by treatment with hot Na₂CO₃ and NaOH solutions, and, in general, alkali-reagents have been used to dissolve X-ray amorphous aluminosilicates, free silica and alumina. In contrast, acids have been employed for the selective dissolution of crystalline material. Digestion with dilute Na₂CO₃ solution has been considered to remove the amorphous silicious material (Jackson 1956), although Hashimato and Jackson (1960) have stated that frequently amorphous inorganic material was not dissolved completely with this reagent. They consequently studied the differential dissolution of clay with NaOH and found that substantial amounts of allophane, free silica, and alumina were brought into solution by boiling for 2.5 min with 0.5N NaOH Solution. Mitchell and Farmer (1962), however, successfully removed highly hydrated amorphous inorganic material from the clay fraction of certain brown forest soils and grey-brown podzolic soils by successive digestions on a steam bath with 5% Na₂CO₃ solution and a New Zealand allophanic soil clay was also largely dissolved by this treatment (Follett et al. 1965).

Allophane is an amorphous aluminosilicate that is a major constituent of soil clays derived from volcanic ash. Lai and Swindale (1969) defined allophones as hydrated aluminosilicates amorphous to X-rays without ordered crystal structures. These are also drawing attention in different parts of the world owing to their tremendous surface reactions governing different important soil properties despite their presence in very small quantities. For many years, reliable quantitative determination of this component in soil was hampered by allophane, a somewhat vague and poorly defined term (Fey and Roux 1975). It seems probable that this situation may have arisen because of the poor specificity of various chemical reagents used for extracting amorphous material. Thus, conventional boiling 0.5N NaOH treatment (Hashimoto and Jackson 1960) will partially dissolve, along with an amorphous aluminosilicate component, crystalline clays such as nontronite, kaolinite and halloysite (Fey and Roux 1975).

Amorphous aluminosilicates are not amenable to quantitative determination by established instrumental techniques such as infrared and X-ray fluorescence spectroscopy, thermal analysis and electron microscopy. However, these are important tools for their characterization. Experience has shown that for all its theoretical limitations and empiricism, differential or selective chemical dissolution still offers the best and possibly only means of estimating the allophane content of polymineralic materials such as soil.

Although several procedures for estimating the allophane content of soils have been proposed and used, rigorous quantitative determination remains a problem. Basically, the problem arises from (i) a lack of precision in the concept and definition of the material to which the term allophane may appropriately be applied and (ii) a degree of empiricism necessarily attaching to any analytical procedure since, as far as is known, materials described as allophane lack unique reactions whereby they may be unambiguously distinguished from other finely particulate soil components together with which they usually occur.

To find a suitable extractant for quantitative estimation of amorphous materials, three extractants were selected from the existing commonly used methods. One is 0.5N NaOH (flash boiling for 2.5 mts) proposed by Hashimoto and Jackson (1960). The second extractant is the 5% cold and hot Na₂CO₃ treatment proposed by Follett et al. (1965). The third and last one is acid ammonium oxalate (pH 3), which was proposed by Fey and Roux (1975). The selection of one extractant and its efficiency in quantitative estimation may be carried out either by selecting materials that are completely amorphous in nature or by selecting crystalline materials devoid of any amorphous materials. The latter method was chosen to determine the efficiency of a single method out of the selected three extractants.

Dissolved constituents were calculated to estimate the amorphous materials in soil, according to de Villiers (1971) and Alexiades and Jackson (1966). The results of the extraction of amorphous constituents by different methods are presented in table 4. In all the cases, however, the percentage of amorphous material was less when de Villiers' method was followed, as is evident from the milder extractant (acid ammonium oxalate).

When the methods were applied for pure kaolinite, mica and montmorillonite, it was observed that 0.5N NaOH and 5% Na₂CO₃, both cold and hot, extracted silica as well as alumina from all these three minerals except in the case of montmorillonite, acid oxalate treatment failed to extract any silica or alumina (Table 4). This is expected as these minerals are purely crystalline and do not contain amorphous materials. It shows that oxalate is a milder extractant and does not attack the crystalline component. In other words, it dissolves only the noncrystalline component. Logically, oxalate should be selected from all the extractants tried for selective dissolution of amorphous constituents without affecting the crystalline part.

The amorphous substances in all the five Entisols (Bentlu, Mohitnagar, Karnall, Katwa and Jorhat) varied from 0.002 - 0.006% (acid oxalate), in 0.5N NaOH the values observed were 0.408, 0,459, 0.255, 0.043 and 0.357% respectively while in case of Na₂CO₃ the corresponding values were 0.187, 0.259, 0.116, 0.072 and 0.173% respectively. Calculations based on Alexiades and Jackson's (1966) method gave even higher values with the same extractants. These values were 0.800, 0.811, 0.766, 0.055 and 0.811% (0.5N NaOH) and 0.449, 0.659, 0.182, 0.167 and 0.321% in the same order of soils as mentioned earlier (Na₂CO₃).

SI No.	Minerals/Soils	0.5 N NaOH					Acid Amm. Oxalate (pH 3)				5 % Na ₂ CO ₃					
		SiO ₂ ,	Al ₂ O ₃	Fe ₂ O ₃	A	llophane	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Allophane	Н	lot	Co	ld	Allop	hane
					(1)**	(2)+	%	%	%	(1)**	SiO ₂	Al ₂ O ₃	SiO ₂	Al ₂ O ₃	(1)**	(2)+
			%	%	%	%				%	%	%	%	%	%	%
1.	Kaolinite	1.33		0.085							0.005	0.003	0.0007	0.615		
2.	Mica	1.11		0.195							0.056	0.343	0.013	0.450		ł
3.	Montmorillonite	1.40		0.195			0.003	-	-		0.004	0.005	0.015	0.363		
1.	Bentlu	0.64	0.08	0.32	0.408	0.800	0.001	0.0002	0.56	0.006	0.07	0.133	0.06	0.141	0.187	0.449
2.	Mohitnagar	0.64	0.09	0.12	0.459	0.811	0.005	0.0004	0.27	0.002	0.139	0.10	0.10	0.263	0.259	0.659
3.	Karnal	0.64	0.05	0.16	0.255	0.766	0.001	0.0004	0.48	0.002	0.04	0.082	0.04	0.074	0.116	0.182
4.	Katwa	0.03	0.02	0.19	0.043	0.055	0.001	0.0002	0.70	0.001	0.02	0.074	0.03	0.072	0.072	0.167
5.	Jorhat	0.66	0.07	0.09	0.357	0.811	0.001	0.0007	0.32	0.003	0.05	0.072	0.07	0.097	0.173	0.321
6.	Henningkonglwa	0.37	0.02	0.19	0.102	0.433	0.002	0.0014	1.29	0.007	0.04	0.079	0.04	0.111	0.116	0.220
7.	Palampur	0.03	0.09	0.24	0.043	0.133	0.002	0.0004	0.56	0.002	0.05	0.139	0.08	0.210	0.187	0.537
8.	Naddi	0.90	0.05	0.64	0.255	1.055	0.001	0.0008	1.29	0.004	0.04	0.097	0.06	0.082	0.144	0.310
9.	Chikballapur	1.78	0.39	0.80	1.991	2.411	0.002	0.0004	1.93	0.002	0.09	0.164	0.08	0.164	0.245	0.553
10.	Indore	0.50	0.05	0.32	0.255	0.611	0.004	0.0008	1.28	0.004	0.05	0.110	0.07	0.075	0.173	0.339
11.	Nandyal	0.43	0.01	0.31	0.051	0.488	0.004	0.0002	1.02	0.001	0.05	0.092	0.07	0.067	0.173	0.310
12.	Siraguppa	0.50	0.01	0.25	0.051	0.566	0.005	0.0007	0.32	0.003	0.06	0.099	0.11	0.104	0.244	0.414
13.	Kohima	0.64	0.02	0.19	0.102	0.733	0.001	0.0004	0.59	0.002	0.04	0.115	0.06	0.210	0.144	0.472
14.	Tamanda	0.19	0.11	0.49	0.274	0.333	0.001	0.00008	1.02	0.004	0.05	0.115	0.06	0.144	0.158	0.412

Table 4. Effect of various chemical extractants on dissolution of SiO₂, Al₂O₃ and Fe₂O₃ from different minerals and soils

(1) **Allophane % = (x + 0.282x)/0.89 (when SiO₂/Al₂O₃ molar ratio < 6.0)

(2) +Allophane % = (% SiO2 + % Al2O3)/0.9 (Allexiades and

Jackson, 1966)

Or

**Allophane % = (y + 0.282y)/0.89 (when SiO₂/Al₂O₃ molar ratio > 6.0), Where x = % SiO₂ and y = % Al₂O₃ (de Villiers, 1971)

When values from Henningkonglwa (Nagaland), Palampur, Naddi and Chikballapur (All Alfisols) were compared, the similar observations were noted. The values for acid oxalate were 0.007, 0.002, 0.004 and 0.002%, respectively. For 0.5N NaOH, 0.102, 0.043, 0.255 and 1.991% and for 5% Na₂CO₃ the values were 0.116, 0.187, 0.144 and 0.245%, respectively. These results suggest again that acid oxalate is a better extractant than other methods. Data calculated according to Alexiades and Jackson (1966) for amorphous constituents were found to be very high. These were 0.433, 0.133, 1.055 and 2.411% for 0.5N NaOH and 0.220, 0.537, 0.310 and 0.553% for 5% Na₂CO₃ in the same order as mentioned earlier (Table 4).

When the data for three black soils for amorphous materials were compared, acid ammonium oxalate was observed to give the lowest values; these were 0.004, 0.001 and 0.003% for Indore, Nandyal and Siraguppa soils, the corresponding values in 0.5N NaOH were 0.255, 0.051 and 0.051% and in 5% Na₂CO₃ were 0.173, 0.173 and 0.244% respectively. This suggests that oxalate extracts the amorphous materials and does not attack the crystalline component common with the two other extractants. This is why higher values are observed in the case of 0.5N NaOH and 5% Na₂CO₃.

In the case of two Ultisols from Kohima and Tamanda (0rissa), amorphous substances had very low values (0.002 and 0.004%, respectively) when extracted with acid ammonium oxalate. The corresponding values for 0.5N NaOH were 0.102 and 0.274%, while for 5% Na₂CO₃ these were 0.144 and 0.158% respectively. Higher values were, however, obtained using Alexiades and Jackson's method for calculation; these were 0.733 and 2.411% for 0.5N NaOH and 0.472 and 0. 412% for 5% Na₂CO₃.

The above results suggest that acid ammonium Oxalate is a better extractant, particularly when the data on extraction of amorphous constituent from standard clay minerals are considered. Oxalate extractant is milder and less destructive. Amounts of silica and alumina dissolved by oxalate from different soils are lower than those removed by NaOH and Na₂CO₃. This evidence might suggest that the former extractant is less efficient than the latter. On the other hand, the NaOH and Na₂CO₃-soluble fraction also will represent variable dissolution from sources such as chloritized 2:1 layer silicate and poorly ordered kaolinite and halloysite (Fey and Roux 1977). For these reasons, oxalate values are considered the most meaningful of the two in terms of amorphous materials.

It should also be mentioned in this connection that a significant advantage of oxalate over other commonly used extractants is its additional specificity for amorphous ("active") iron oxides, which are also extracted in the same treatment (Table 4). The oxalate-extracted iron oxides in Entisols were 0.56, 0.27, 0.48, 0.70 and 0.32% for Bentlu, Mohitnagar, Katwa And Jorhat samples. In Alfisols the values observed were 1.29% (Henningkonglwa), 0.56% (Palampur), 1.29% (Naddi) and 1.93% (chikballapur).

The Vertisols from Indore, Nandyal and Siraguppa contained 1.28, 1.02 and 0.32% of oxalate soluble iron oxides. The Kohima and Tamanda samples (Ultisols) contained 0.59% and 1.02% respectively.

Large Entisols contained relatively less oxalate soluble iron oxides while Alfisols and Vertisols were found to have greater Fe₂O₃. Among Ultisols, Tamanda had relatively higher amount of this amorphous iron oxides.

4.c) Characterization of humic acid

1. Carbon content

Among 5 Entisols studied, the Walkley-Black carbon was maximum in Bentlu (55.29%) followed by Mohitnagar (43.06%), Karnal (42.13%), Katwa (40.56%) and Jorhat (33.44%) (Table 5).

The value of alfisols was lower except in Chikballapur red soil. Organic carbon values were 34.17, 33.86, 31.71 and 40.05% for Henningkonglwa, Palampur, Naddi and Chikballapur, respectively.

The organic carbon values for three Vertisols from Indore, Nandyal and Siraguppa were 45.24, 48.34 and 45.24% respectively.

The corresponding values in Kohima and Tamanda (both Ultisols) were 39.90 and 34.50% respectively.

Similar values of organic carbon, as observed in Bentlu (Entisol) and Nandyal (Vertisol) were reported for humic acids while studying alluvial soils (Sachdev and Deb 1982), brown forest and alluvial soils (Chatterjee and Ghosh 1981). The relatively higher values for humic acids reported by these authors differ from typical unhydrolysed humic acids by having a lower carbon, as observed in most cases (Russell 1973).

2. Nitrogen content

In 5 Entisols from Bentlu, Mohitnagar, Karnal, Katwa and Jorhat, the nitrogen content in humic acids were 4.18, 4.03, 3.60, 4.82 and 3.13%, respectively (Table 5).

The corresponding values in Henningkonglwa, Palampur, Naddi and Chikballapur were 2.93, 2.59, 3.92 and 2.68% respectively.

Among three Vertisols, maximum N was found in the Indore sample (3.87%) followed by Nandyal (3.09%) and Siraguppa (2.94%).

Sl. No.	Soils	Walkley-	Nitrogen C/N		Optical	E4/E6	
		Black carbon		Ratio	465 nm (E ₄)	665 nm	ratio
		(%)				(E_6)	
1.	Bentlu	55.29	4.18	13.23	0.205	0.045	4.55
2.	Mohitnagar	43.06	4.03	10.68	0.470	0.115	4.08
3.	Karnal	42.13	3.60	11.70	0.320	0.090	3.55
4.	Katwa	40.56	4.82	8.41	0.375	0.085	4.41
5.	Jorhat	33.44	3.13	10.68	0.690	0.185	3.72
6.	Henningkonglwa	34.17	2.93	11.66	0.280	0.065	4.30
7.	Palampur	33.86	2.59	13.07	0.290	0.065	4.46
8.	Naddi	31.71	3.92	8.09	0.715	0.145	4.93
9.	Chikballapur	40.05	2.68	14.94	0.400	0.105	3.80
10.	Indore	45.24	3.87	11.69	0.585	0.120	4.87
11.	Nandyal	48.34	3.09	15.64	0.490	0.090	5.44
12.	Siraguppa	45.24	2.94	15.37	0.390	0.070	5.57
13.	Kohima	39.90	2.85	14.00	0.270	0.070	3.85
14.	Tamanda	34.50	2.23	15.47	0.030	0.005	6.00

Table 5. Some characteristics of humic acids

The two Ultisols from Kohima and Tamanda contained 2.85 and 2.23% N, respectively.

Sachdev and Deb (1982) reported that the value was 2.926% for alluvial soils. The values obtained by Chatterjee and Ghosh (1981) for the brown forest, alluvial, and laterite soils were 4.0, 3.5 and 2.6%, respectively. The nitrogen content ranged from 4.10-5.34% in humic acid extracted from Mollisol, Alfisol and Histosol (Ram and Raman 1981).

3. C:N ratio

The Entisols from Bentlu, Mohitnagar, Karnal, Katwa and Jorhat had a C/N ratio of 13.23, 10.68, 8.41 and 10.68 (Table 5).

In the case of Alsisols, the C/N ratio values were 11.66, 13.07, 8.09 and 11. 24 for Henningkonglwa, Palampur, Naddi and Chikballapur respectively.

The results thus indicate a wider variation in the C:N ratio of humic acid in Entisols and Alfisols compared to that observed in Vertisols and Ultisols. A trend of increasing C:N ratio in the following order is also indicated: Vertisol > Ultisol > Alfisol > Entisol. This trend should, however, be taken only as an indication, and no generalization can be made without obtaining data from more samples.

In Indore, Nandyal and Siraguppa samples, the corresponding values for C/N ratio were 11.69, 15.64 and 15.37, respectively.

The Ultisols from Kohima and Tamanda had the C/N ratio value s of 14.00 and 15.47. These C/N ratio values are supported by the works of Sachdev and Deb (1982), Chatterjee and Ghosh (1981), and Ram and Raman (1981).

4. E4:E6 ratio

Optical densities (OD) were measured at 465 and 665 nm to determine the nature of humic acids. In a particular group of soil and among different groups, there was a large variation in OD values (Table 5). It could be attributed to (i) the degree of condensation of aromatic rings that humic acids contain and (ii) the ratio of carbon in aromatic nuclei to carbon in aliphatic or salicyclic side chains (Kononova 1966).

The lower value of the E₄:E₆ ratio signifies a higher degree of aromatization.

Among 5 Entisols, Bentlu, Katwa and Mohitnagar had relatively higher ratios of 4.55, 4.41 and 4.08, while narrower ratios of 3.55 and 3.72 in Karnal and Jorhat samples suggest a higher degree of aromatization.

In the case of Alfisols, the Chikballapur sample had a narrower ratio of 3.80, while Henningkonglwa, and Palampur Naddi samples had a ratio of 4.30, 4.46 and 4.93, respectively.

In case of Vertisols, Indore had a narrower ratio of 4.87, while the Nandyal and Siraguppa samples had 5.44 and 5.57 values of this ratio. Nevertheless, the values observed in Vertisols were higher than those found in Alfisols and Entisols. Among the 14 samples studied, Karnal, Jorhat, Chikballapur and Kohima had narrower ratios in increasing Order. This suggests a higher degree of aromatization in these samples. Similar results were reported by Gupta et al. (1982).

Among the two Ultisols, Kohima had a relatively narrow ratio of 3.85, while Tamanda had a maximum ratio of 6.00 among all the samples studied. This signifies a relatively lower degree of aromatization of humic acid components in the organic matter of this soil.

Leaving aside the Ultisol of Kohima, the Vertisols and Ultisols with relatively wider E_4/E_6 ratio seem to have lower aromatization. Thus, a lower degree of aromatization is associated with a high degree of soil weathering.

5. Infrared studies

The infrared spectra of humic acid of 5 Entisols are shown in Figs 2 and 3. The band observed at 3400 cm⁻¹ or around this wave number was strong and broad in the five cases. The band in the Jorhat sample was, however, relatively strong. The broadness in the band indicated extensive overlapping of the polymerically bonded-OH groups. The band at 2900 cm⁻¹ was weak in all humic acids. The low absorption in these samples appeared to be due to low aliphatic C-H stress. At around 1700 cm⁻¹, Mohitnagar and Bentlu samples showed an absorption shoulder; in Karnal, Jorhat and Katwa soils, this was relatively better delineated. At this band, low absorption in humic acid of Mohitnagar and Bentlu (Mountain and Foot Hill) soils in comparison to the humic acids of Karnal, Jorhat and Katwa (Alluvial soils) revealed variation in their carboxylic group content. The band at 1638-1640 cm⁻¹ was strong in all cases. This band, however, was broad in Mohitnagar. The strong absorption in this region is due to a higher degree of aromatization. The relatively narrower E_4/E_6 values support this observation. Schnitzer and Khan (1972) reported that C=O groups absorb IR radiation strongly between 1800 and 1600 cm⁻¹ and 1600 and 1400 cm⁻¹. In all five samples, the bands at 1498-1500 cm-1, 1450 cm-1 and 1400 cm-1 were observed due to C=O groups.



Figure 2. Infrared spectra of humic acids (Karnal, Jorhat and Katwa)



Figure 3. Infrared spectra of humic acids (Kohima, Tamanda, Mohitnagar and Bentlu)

The absorption band at 3400 cm⁻¹ was strong and broad for all four humic acids from Alfisols (Fig. 4). The intensity of this band, however, increased in this order: Naddi < Palampur < Chikballapur < Henningkonglwa suggesting the increasing trend of polymeric-OH bond present in these samples. The absorption band at 2900 cm⁻¹ was weak in all the cases except in Naddi, where it was missing. Low absorption IR radiation suggests low aliphatic-CH stress in these samples. The order in which aliphatic-CH groups increased is Chikballapur < Henningkonglwa < Palampur. The band around 1700 cm⁻¹ appeared as a shoulder in Naddi soil, while in the other three soils, the intensity increased in the order of Chikballapur < Henningkonglwa. The differential absorption pattern in this region shows variation in their carboxylic group content. The absorption band at around 1640 cm⁻¹ was relatively strong. The band intensity among this group of soils increased in the order of Naddi < Palampur < Henningkonglwa < Chikballapur. While comparing this band intensity with E₄/E₆ values, the expected relationship of this band (higher degree of aromatization) and the E₄/E₆ ratios was obtained. Henningkonglwa soil was an exception in this regard. The bands observed at 1500 cm⁻¹ and 1400 cm⁻¹ were similar in all the cases except in Palampur soil. Here, the 1500 cm⁻¹ band was relatively weak, suggesting its lesser degree of aromatization when compared with the other three soils.

Fig.5 shows the infrared spectra of three Vertisols from Indore, Siraguppa and Nandyal. The absorption band at 3400 cm⁻¹ was quite strong and broad for all the samples. The intensity increased in the order Siraguppa < Indore < Nandyal. The broadness in this band indicated extensive overlapping of the polymerically bonded- OH groups. The band at 2900 cm⁻¹ was weak in all the cases. The low absorption appeared to be due to low aliphatic-CH stress. Among these three samples, the aliphatic-CH group content increased in this order: Indore = Siraguppa < Nandyal. The band at 1700 cm⁻¹ was due to C=0 groups. This band appeared in all three cases, and no variation could be found in the spectra, suggesting similar carboxylic group content in the humic acid from these three black soils. The band at 1640 cm⁻¹ was strong for the humic acids due to a higher degree of aromatization. The bands observed at 1500 cm⁻¹ and 1400 cm⁻¹ were broad in all the cases.



Figure 4. Infrared spectra of humic acids (Chikballapur, Naddi, Palampur and Henningkonglwa)



Figure 5. Infrared spectra of humic acids (Indore, Siraguppa and Nandyal)

Fig.3 gives the infrared absorption spectra of two Ultisols (Kohima and Tamanda). The band observed at 3400 cm⁻¹ was strong in both cases. The intensity and broadness were higher in Tamanda soil. The broadness in this band indicated extensive overlapping of the polymerically bonded-OH groups. The absorption band at 2900 cm⁻¹ was a shoulder in Kohima soil. The low absorption in this band appeared to be due to low aliphatic-CH stress. This band was missing in Tamanda soil, indicating the absence of an aliphatic-CH band. The band at around 1700 cm⁻¹ was shoulder in the Tamanda sample. It was observed in Kohima soil, indicating their carboxylic group content variation. The 1640 cm⁻¹ absorption band was strong in both cases. However, this appeared relatively with higher intensity in Kohima soil. This is due to a higher degree of aromatization supported by the narrow E_4/E_6 ratio (Table 5). The bands observed at 1500 cm⁻¹, 1450 cm⁻¹ and 1400 cm⁻¹ were similar in both cases. Among the 14 soils, the 2900 cm⁻¹ band (aliphatic-CH) was pronounced in the Nandyal sample; this band appeared as shoulder in Palampur, Jorhat, Karnal, Katwa and Henningkonglwa samples. This indicates that possibly aliphatic-CH groups are present more in the Nandyal sample than others. This band was missing in Naddi and Tamanda samples. The relatively stronger absorption bands in Karnal (Entisol), Jorhat (Entisol), Chikballapur (Alfisol) and Kohima (Ultisol) indicate an abundance of aromatic C=0 groups, which was supported by relatively narrow E₄/E₆ ratios. In other words, this suggests more aromatization in these soils. These observations find support from the works of Sachdev and Deb (1982) and Mukhopadhyay et al. (1982).

4. d) <u>Clay-organic complex</u>

The clay-organic complex has been characterized concerning (1) organic matter content, (2) nitrogen content, (3) specific surface area, (4) cation exchange capacity, (5) potassium fixation capacity, (6) chemical composition, (7) content of amorphous constituents, (8) IR absorption characteristics, (9) morphological features by T.E.M., and (10) content of crystalline constituents by X-ray diffraction analysis. The change in the complex after the removal of organic matter and free oxides and allophanes in succession has also been investigated. The results of these studies are presented below under appropriate headings.

1. Organic matter content (%)

Out of the five Entisols from Bentlu, Mohitnagar, Karnal, and Jorhat, Mohitnagar was observed (Table 6) to have the highest quantity of organic matter (10.88%), followed by Jorhat (6.31%), Bentlu (5.33%), Katwa (3.08%) and Karnal (2.98%). The Mohitnagar soil has been enriched with humus, which comes with washing from the Darjeeling Himalayan region every year (Raychaudhuri 1964). Therefore, it is not surprising that this soil's clay-humus complex has the highest organic matter content amongst all the Entisols. The soil in Jorhat has been formed on Brahmaputra alluvium, which is not rich

in humus content; in fact, the humus accumulation in this soil depends more on the vegetation and rainfall. As a result, the clay-organic complex has a relatively lower organic matter content. The Bentlu soil is, however, from the hilly area where both climatic conditions and vegetation favoured a higher accumulation of organic matter. Both Katwa and Karnal represent soils on old alluvium. Katwa, however, has high rainfall; the deposit is clayey, and the soil is used mainly for paddy cultivation. This condition apparently has favoured higher organic matter accumulation in the clay-organic complexes in Katwa soil compared to Karnal soil, which receives low rainfall, has sandy loam texture, and is used mainly for wheat cultivation.

Out of the four Alfisols from Henningkonglva, Palampur, Naddi and Chikballapur, the organic matter content was maximum (8.65%) in the Palampur clay-organic complex, and it was lowest in Chikballapur clay-organic complex. The Chikballapur soil is from a semi-arid region. It has developed under conditions that are not conducive to the accumulation of humus to the extent that it is possible in the other three soils of this group. The other three soils are from mountain and hilly regions where vegetation and climatic conditions are relatively favourable for slow humification and complex formation with inorganic constituents. This possibly explains why the clay-organic complex from Alfisols of hills has a higher organic content than the Semi-arid plain.

Among the three Vertisol samples, the clay-organic complex isolated for Nandyal had a maximum of 3.40% organic matter; 0.55% and 1.12% were the values for Indore and Siraguppa samples, respectively (Table 6).

Konima and Tamanda (both Ultisols) had 6.15% and 4.81% organic matter (Table 6). Because of forest cover under high rainfall, the surface soil has become enriched with organic matter. The high content of organic matter in the clay-humus complex of these two soils is otherwise unexpected, as Ultisols rarely is likely to yield such clay-organic complex.

2. Total nitrogen content (%)

Total N in an untreated sample from Bentlu (0.40%) decreased to 0.24% after removing organic matter, and on peroxide -CBD-oxalate treatment, it registered 0.24% N (Table 7). It, therefore, appears that even after peroxide treatment, appreciable organic matter remains associated with iron oxide and amorphous constituents in the clay-organic complex of this soil. Mohitnagar (0.69%), Karnal (0.64%), Katwa (0.62%) and Jorhat (0.79%) samples contained relatively higher N percentages in untreated samples. The N content in the peroxide-treated sample decreased significantly in all these samples. The decrease was greater in Mohitnagar and Jorhat samples. Among the Entisols clay-organic complex, all the samples have appreciable organic matter content associated with iron oxide and amorphous material.

In the Henningkonglwa sample, the nitrogen content decreased from 0.37% in untreated samples to 0.29% in hydrogen peroxide-treated samples. Removal of iron oxides and amorphous materials did not result in any difference in nitrogen content. This indicates that very little or no organic matter remained associated with the soil's iron oxides and amorphous constituents after peroxide treatment.

Palampur and Naddi samples had a similar percentage of nitrogen (0.20 and 0.23%, respectively) in the untreated complex. However, the decrease in nitrogen content due to the peroxide treatment was greater in Palampur samples. The peroxide-CBD- oxalate treatment resulted in no change in nitrogen content. The clay-organic complex of these soils also behaved like that of Henningkonglwa samples.

CL N	G 1	
SI. No.	Soils	Organic matter (%)
1.	Bentlu	5.33
2.	Mohitnagar	10.88
3.	Karnal	2.98
4.	Katwa	3.08
5.	Jorhat	6.31
6.	Henningkonglwa	5.83
7.	Palampur	8.65
8.	Naddi	3.50
9.	Chikballapur	2.95
10.	Indore	0.55
11.	Nandyal	3.40
12.	Siraguppa	1.12
13.	Kohima	6.15
14.	Tamanda	4.81

Table 6. Organic matter content of clay-organic complex
Chikballapur sample with 0. 45% N decreased to 0.33% after peroxide treatment and 0.26% after peroxide-CBD-oxalate treatment.

In all three Vertisol samples from Indore, Nandyal and Siraguppa, nitrogen content in untreated samples (0.47, 0.29 and 0.79, respectively) decreased as the clay-organic complex had the treatments of H_2O_2 and H_2O_2 -CBD-oxalate. The decrease was more conspicuous in the Indore sample as the complex was treated with H202. A consistent decrease was observed due to both treatments in Siraguppa samples. In Indore and Nandyal samples, removing iron oxides and amorphous materials produced no change in nitrogen content. The values for nitrogen content of the cleaned samples were 0.29, 0.21 and 0.29%, respectively (Table 7).

Kohima and Tamanda (Ultisols) samples had 0.33 and 0.59% N in an untreated complex, which came down to 0.31 and 0.54% for peroxide treatment. Removal of free oxides and amorphous materials resulted in no change in Koh ima sample; in Tamanda, the value decreased to 0.30%.

Out of the fourteen samples studied, Siraguppa (Vertisol), Mohitnagar (Entisol), Karnal (Entisol) and Jorhat (Entisol) samples had higher values of total N content. All samples were found to lose N on peroxide treatment. The N content decreased in six samples and remained unchanged in eight samples due to the CBD-oxalate treatments of the peroxide-treated complex. The most interesting aspect of this analysis was that even after CBD-oxalate treatment of the peroxide-treated complex, a fairly high amount of nitrogen was still retained, though the content varied from soil to soil. This nitrogen obviously came from the organic matter that was not oxidised by the peroxide treatment and was not removed in the CBD-oxalate treatment. It can, therefore, be considered strongly bound and not easily oxidisable organic matter involved in the complex formation. The evidence of such organic residues on clay samples has also been noted in the electron microscopy of the samples.

A close look at the table for per cent reduction in total N content for Entisols revealed that Bentlu, Mohitnagar, Katwa and Jorhat samples had greater reductions of 40.00, 60.86, 40.30 and 36.70 (Table 7). Karnal sample had relatively less reduction of 14.06 when organic matter was removed. When percent reduction after removing free iron oxides and amorphous material was calculated, it was observed that in Mohitnagar, Karnal and Jorhat samples, the reduction was 25.92, 43.70 and 29.11%, respectively. In the Bentlu and Katwa samples, no change in N content was observed when compared with values in peroxidized samples.

Sl. No.	Soils	Nitroge	Reduction (%)	in N content		
						due to
		Untreated	Peroxide treated	Peroxide CBD- Oxalate treated	Peroxidation	Peroxide CBD- Oxalate treatment
		а	b	с	[a-b/a] * 100	[b-c/a] * 100
1.	Bentlu	0.40	0.24	0.24	40.00	
2.	Mohitnagar	0.69	0.27	0.20	60.86	25.92
3.	Karnal	0.64	0.55	0.27	14.06	43.70
4.	Katwa	0.62	0.37	0.37	40.30	
5.	Jorhat	0.79	0.50	0.27	36.70	29.11
6.	Henningkonglwa	0.37	0.29	0.29	21.62	
7.	Palampur	0.20	0.12	0.12	40.00	
8.	Naddi	0.23	0.18	0.18	21.74	
9.	Chikballapur	0.45	0.33	0.26	26.66	21.21
10.	Indore	0.47	0.29	0.29	38.30	
11.	Nandyal	0.29	0.21	0.21	27.58	
12.	Siraguppa	0.79	0.60	0.29	24.05	39.22
13.	Kohima	0.33	0.31	0.31	6.06	
14.	Tamanda	0.59	0.54	0.30	8.47	40.70

Table 7. Total nitrogen content of clay-organic complex with different treatments

In Alfisols, the reduction values were more or less similar in Henningkonglwa (21.62%), Naddi (21.74%) and Chikballapur (26.66%). In the Palampur sample, this reduction was due to organic matter removal being 40.00%. However, removing free iron oxides and amorphous materials yielded no change in N content in these soils except in the Chikballapur sample; here, the per cent reduction value was 21.21.

Among Vertisols, the reduction in N values in peroxidized samples was 38.30, 27.58 and 24.05%, respectively, for Indore, Nandyal and Siraguppa. The CBD-oxalate treatment in the peroxidized sample resulted in a reduction of 39.22% only in the Siraguppa sample. Kohima and Tamanda had low reductions of 6.06 and 8.47% in the peroxidized sample; in the former sample, however, no change was noted in N content after CBD-oxalate treatment. The latter treatment reduced the value of Tamanda to 40.70%.

Out of the 14 soils studied, Katwa, Jorhat and Siraguppa samples retained relatively higher amounts of N even after total cleaning with H_20_2 -CBD-oxalate—besides, all other samples retained N in the cleaned samples in variable amounts. As already mentioned, the source of this N is organic matter, it suggests that even after several treatments, the organic matter remained associated with these samples in forming a complex with the mineral constituents of the soils.

3. Specific surface area

Out of 5 Entisols, Katwa (634 m²/g) and Mohitnagar (537 m²/g) had relatively higher values for specific surface area (Table 8) followed by Jorhat (494 m²/g), Karnal (476 m²/g) and Bentlu (470 m²/g). Removal of organic matter resulted in an overall decrease in these values. The decrease was maximum in the case of the Mohitnagar (organic matter content 10.88%) sample. The specific surface area values in the peroxide-CBD-oxalate treatment samples decreased in Bentlu and Mohitnagar, while they increased in the other three cases. Thus, it is apparent that the removal of cementing materials, coatings and free Fe/Al oxides may lead to either an increase or decrease in the specific surface area depending on whether the specific surface area of the material removed is higher or lower than the specific surface area exposed as a result of the removal of those materials.

C1	G	C		(2 1)			
SI.	Soils	Spe	ecific surface a	reas (m ² g ⁻¹)	Reduction (%)) in the Specific surface	
No.				area content due to			
		Untreated	Peroxide-	Peroxide-CBD-	Peroxidation	Peroxide-CBD-	
			treated	oxalate treated		oxalate treatment	
		а	b	с	[a-b/a] * 100	[b-c/a] * 100	
1	Bentlu	470	270	139	-42.55	-48.52	
2	Mohitnagar	537	200	121	-62.75	-39.50	
3	Karnal	476	350	373	-24.36	+6.57	
4	Katwa	634	625	769	-1.42	+18.72	
5	Jorhat	494	460	690	-6.88	+50.00	
6	Henningkonglwa	374	209	121	-44.12	-42.10	
7	Palampur	500	327	218	-45.40	-33.33	
8	Naddi	350	400	562	+14.28	+9.50	
9	Chikballapur	484	216	56	-55.37	-74.07	
1	Indore	913	814	790	-10.84	-2.95	
1	Nandyal	1073	854	790	-20.41	-7.49	
1	Siraguppa	999	895	820	-10.41	-8.38	
1	Kohima	486	428	460	-11.93	+7.47	
1	Tamanda	437	349	149	-20.14	-57.30	

Table 8. Specific surface areas of clay-organic complex with different treatments

The 4 Alfisol samples from Henningkonglwa, Palampur, Naddi and Chikballapur were observed to have a specific surface area of 374, 500, 350 and 484 m²/g when no treatment was given; the corresponding values in peroxide-treated samples were 209, 327, 400 and 216 m²/g respectively (Table 8). The reduction in surface area values directly relates to organic matter content in the order of Palampur, Henningkonglwa and Naddi. However, in the case of Chikballapur samples, the reduction was maximum out of these 4 Alfisols. When the samples were deferrated and again treated with acid ammonium oxalate, the total surface area in one sample increased and decreased in others. In Naddi samples, the values increased to 562 m²/g. In all other cases, the values decreased with the maximum fall in specific surface area in Chikballapur, followed by Palampur and Henningkonglwa. When this decrease in specific area values were compared with amorphous content, it was observed that more amorphous materials were associated with a greater fall in the surface area, as was expected from this treatment. Besides, the mineralogical composition of these clays also showed general agreement with the surface area obtained for the cleaned clays.

As expected (from the mineralogical data), the three Vertisol samples had a very high total surface area of 913, 999 and 1073 m^2/g in Indore, Siraguppa and Nandyal, respectively (Table 8). Removal of organic matter decreased the values to 814, 895 and 854 m^2/g in those samples. This had a direct correlation to organic matter content in the samples. Nandyal had the maximum amount of organic matter, and its surface area decreased by the maximum number of units. When surface area was measured in peroxide-dithionite-oxalate treated samples, the value was still reduced. The dithionite and oxalate treatments removed free iron oxides and amorphous materials, so this continuous decrease in total surface area suggests a possible interaction between organic matter, amorphous materials, and crystalline minerals. The decrease in surface area also shows how these two soil constituents influence the overall surface area in the complex. It should be mentioned that these three samples have a similar mineralogy (c.f. quantitative mineralogy), which is also reflected in the total surface area of the cleaned sample.

In the case of Kohima and Tamanda samples (Ultisols), the surface areas in untreated samples were 486 and 437 m²/g. In both cases, the values decreased to 428 and 349 m²/g when organic matter was removed from the samples. Compared to the overall reduction in specific surface area values observed in Alfisols, the reduction was much less with peroxide treatment. In both cases, however, further removal of free iron oxides and amorphous materials resulted in either an increase or decrease in specific surface area. The increase may be due to removing oxide and amorphous coating from the mineral surface, which exposes more surface area than the materials removed. Besides, the presence of residues of diatoms must (cf.electron micrographs of Kohima samples, (Plate 9c) have increased the surface area as the pores which were initially filled with OM and iron oxides were subsequently opened up by the H₂O₂, CBD and oxalate treatments. Otherwise, from the mineral make up (cf. quantitative

mineralogy, Table 20) of Kohima sample, much lower surface area is expected for this sample on successive treatments.

CBD-oxalate treatment removes the cementing iron oxide and allophonic material, which have highly variable surface areas depending on their composition and particle size. Removal of these materials exposes new surfaces of clay minerals. Whether the effect of CBD-oxalate treatment will increase or decrease in the surface area depends on the resultant impact of these two opposite processes, viz. (i) removal of material with high surface area and (ii) exposure of new surfaces. If the surface area of the material removed is higher than the new surfaces exposed, the resultant effect is decreased, and *vice versa*.

The increase in surface area in Karnal, Katwa and Jorhat samples may be due to the exposure of minerals with higher surface area (vermiculite present in Karnal clay, smectite in case of Katwa clay) and the presence of diatomaceous materials (cf. electron-micrograph of Jorhat samples, Plates 4e, f and 5a). The decrease may be due to the simple effect of removing materials (oxides and amorphous substances) with very high surface area.

Removal of organic matter in all the cases resulted in a decrease in total surface area values. Naddi sample was the only exception. This reduction was more conspicuous in Bentlu, Mohitnagar, Karnal (Entisols), Henningkonglwa, Palampur, Chikballapur (Alfisols), and all three Vertisols. When free oxides and amorphous materials were removed, the samples were found to have less area values as compared with the values observed in peroxidized samples; however, further increases in specific surface area values were observed in Karnal, Katwa, Jorhat (Entisol), Naddi (Alfisol) and Kohima (Ultisol).

By determining the changes in the specific surface areas brought about by the treatments with peroxide and peroxide-dithionite-oxalate, the resultant effect of any increase due to the removal of cementing materials and losses due to the removal of organic matter and discrete Fe particles is obtained. Thus, if iron oxides and/or organic matter were acting as cement, the decreasing effect of their removal on the surface area would be counteracted by the release of surface area due to the dispersal of discrete clay particles constituting the clay-sized aggregates. Deshpande et al. (1968) obtained both an increase and decrease in clays' total specific surface area before and after deferration.

SL No.	Soils			Mineral	Composition (%)			
51. 1 10.		Smectite	Vermiculite	Chlorite	Interstratified minerals	Mica	Kaolinite	Quartz
1.	Bentlu			7	8	56	25	traces
2.	Mohitnagar	-	-	17	29	40	10	4
3.	Karnal		4			84	11	traces
4.	Katwa	9		19	13	47	12	
5.	Jorhat			19	17	33	31	
6.	Henningkonglwa			6	25	42	24	3
7.	Palampur			16	6	54	12	traces
8.	Naddi	Traces		10	4	58	23	Traces
9.	Chikballapur					23	77	
10.	Indore	52		15	-	30	3	
11.	Nandyal	87				7	6	traces
12.	Siraguppa	70		19		-	11	
13.	Kohima			10	40	15	25	10
14.	Tamanda			6	20	25	44	5

Table	20.	Minera	alogy	of the	peroxide	-CBD-	oxalate	treated	comp	olex
	-		0,		1				1	

Fripiat and Gastuche (1952) determined the change due to successive treatments with acid oxalate in the specific surface areas of the clays from red earth (Congo). In each case, the specific surface area decreased due to removing small iron oxide (goethite and hematite) crystals. Further treatments lead to an increase, in the case of one of the samples, to a value slightly greater than that of the untreated material. The increase was attributed to the removal of relatively resistant iron-oxide film.

4. <u>Cation exchange capacity</u>

The CEC was found to be 146.3, 130.9 and 86.8 me/100 g for the three Vertisols from Indore, Nandyal and Siraguppa, respectively (Table 9). The values of Henningkonglwa, Palampur and Naddi (Alfisols) were 95, 40 and 41.6 me/100 g, respectively. Tamanda sample gave the lowest value of 23.2 me/100 g, and Chikballapur soils gave the highest value of 152.6 me/100g.

Organic matter removal from the complex yielded lower values of CEC except in Nandyal, Henningkonglwa, Tamanda and Katwa soils. Different authors have suggested that, while discovering the contribution of organic matter to cation exchange capacity, some exchange sites are only potentially present on mineral surfaces and do not operate if blocked by the organic matter. Removal of the organic matter may, therefore, increase the exchange capacity.

After removing free iron oxides and amorphous constituents, the complex was left with only the clay minerals. The cation exchange capacity for the three Vertisols was found to be 77.2, 66.9 and 82.9 me/100 g, respectively as is expected considering the mineralogical composition of these soil clays. The overall treatment effect given by the difference of CF (clay- organic complex) and POTCF values indicated that it was more in Indore soils. However, the maximum effect for all the treatments was observed in Chikballapur and Mohitnagar samples. The relative contribution of these two samples was different. For Chikballapur, the impact of peroxide treatment was greater than that of H_20_2 -CBD-oxalate treatment. In Mohitnagar samples, the opposite result was observed.

In Palampur, Naddi and Bentlu samples, the relative contribution of CEC of free oxides and amorphous materials seemed greater than that of organic matter. The former two samples suffered a decrease in CEC values after peroxide treatment. As expected, the CEC values for the cleaned clay of these three samples were similar (22.2-23.9 me/100 g), considering similar mineralogical composition and the amount of clay minerals present in these samples. The high values of CEC for the Bentlu complex (without treatment) and relatively low values of the other two samples could not be correlated with the amount of organic matter present in these three samples.

SI.	Soils		CEC (me/10	0 g)	Change in CEC (me/100 g) due to			
No.		Untrea Peroxide-		Peroxide-	Peroxidation	Peroxide-	Overall	
		ted	treated	CBD- oxalate		CBD-	treatment	
				treated		oxalate	effect	
						treatment		
		а	b	с	a-b	b-c	a-c	
1.	Bentlu	75.7	52.2	23.9	-23.5	-28.3	-51.8	
2.	Mohitnagar	140.8	94.8	28.9	-46.0	-65.9	-111.9	
3.	Karnal	93.9	59.2	38.5	-34.7	-20.7	-55.4	
4.	Katwa	55.9	64.6	27.6	+8.7	-37.0	-28.3	
5.	Jorhat	45.7	5.8	27.1	+0.1	-18.7	-18.6	
6.	Henningkonglwa	95.0	120.6	31.6	+25.6	-89.0	-63.4	
7.	Palampur	40.0	41.0	23.3	+1.0	-17.7	-16.7	
8.	Naddi	41.6	59.1	22.2	+18.5	-36.9	-19.4	
9.	Chikballapur	152.6	57.0	15.5	-95.6	-41.6	137.1	
10.	Indore	146.3	124.2	77.2	-22.1	-47.0	-69.1	
11.	Nandyal	86.3	102.5	66.9	+15.7	-35.6	19.9	
12.	Siraguppa	130.9	130.4	82.4	-0.5	-48.0	-48.5	
13.	Kohima	26.1	20.5	20.5	-5.6	0	-5.6	
14.	Tamanda	23.2	52.6	16.2	+29.4	-36.4	-7.0	

Table 9. Cation exchange capacity (CEC) of clay-organic complex with different treatments

The CEC values increased after peroxide treatment in Nandyal, Henningkonglwa, Palampur, Naddi, Tamanda and Katwa samples, of which Henningkonglwa and Tamanda samples registered a maximum increase in CEC values. Considering very low values of CEC in the untreated complex and then an increase in CEC values (more than double) after removing organic matter and finally attaining a value of 16.2 me/100 g (even less than that in the untreated complex) suggested that the free oxides and arnorphous materials were complexed with organic matter, which after peroxide treatment exposed a lot of surface area and exchange sites, subsequently as the free oxides and allophones were removed by CBD-Oxalate treatment, CEC decreased. The same explanation may hold good in the case of Henningkonglwa samples.

In Jorhat samples, the values of CEC changed only slightly (by 0.1 unit) after peroxide treatment (Table 9). For Katwa samples, the value increased when organic matter was removed. In both the samples, the decrease in CEC values after H202- CBD - oxalate treatment was conspicuous over peroxide treatment. The CEC values decreased stepwise after the treatments in the Karnal and Kohima samples. No change in CEC was observed for Kohima samples after removing free oxides and amorphous materials.

It isn't easy to assess the relative contribution of organic matter and clay to the CEC of soil because separating the two fractions alters their behaviour. The two fractions do not act independently because at least part of the OM is closely bound together as organo-mineral complexes. The interaction causes inactivation of exchange sites which become reactivated when the fractions are separated. Gessa et al. (1978) have also drawn similar conclusions. The fall in CEC values after peroxidation points to the fact that the reactivation of exchange sites of inorganic components could not compensate for the loss of exchange sites due to organic matter removal; hence, the resultant effect is a fall in the total CEC value. This was the case with Indore, Kohima, Bentlu, Mohitnagar, Chikballapur and Karnal samples. On many occasions, peroxidation has resulted in an insignificant change in CEC values over no treatment or no change (e.g. Jorhat, Palampur samples). In these complexes, the association of organic matter and amorphous materials was found to be more common (cf. electromicroscopic studies). In cases where montmorillonite-type minerals dominate, removing organic matter may expose charge sites increasing the CEC values. An example of such a phenomenon is found in Nandyal and Katwa samples. Similarly, removing organic matter may expose the exchange sites of amorphous materials and free iron oxides, contributing to CEC values. This contribution may often lead to CEC values surpassing those observed in samples without treatment. At the same time, the rest of the samples support the explanation given earlier for the increase in CEC values in peroxidized samples.

If we look at the table, the overall treatment effects show that except in Kohima and Tamanda samples, the removal of organic matter, iron oxides and amorphous materials resulted in a greater

change in CEC value, suggesting the tremendous influence these materials have on CEC of the complex (Table 9). The decreases in CEC values in cleaned samples are expected because iron oxides and amorphous materials had their shares in the overall exchange capacities of the complex. Removing iron oxides did not increase negative charge in several soils, including a wide variety of red, tropical soils (Deshpande et al. 1964). The fact that cation exchange capacities of soils can usually be related to the clay mineralogy, high in soils containing vermiculite and montmorillonite, moderate to low in soils containing mica, and low in soils containing kaolinite suggests that they are more the exception than the rule. For the samples shown in Kohima and Tamanda, the removal of surface coatings did not make a very great change in the charge characteristics, indicating that the crust and underlying material are similar in composition.

5. <u>K fixation capacity</u>

Table 10 gives the K fixation capacity of the clay organic complex with different treatments. The 5 Entisols from Bentlu, Mohitnagar, Karnal, Katwa and Jorhat had the K fixation capacity of 3.80, 0.12, 9.67 3.25 and 0.81 mg/g when no treatment was given. The values increased in all the cases in peroxidized samples. The fixation was 17.76, 2.39, 26.67, 5.20 and 2.11 mg/g. This is well in conformity with the fact that organic matter generally blocks or reduces potassium fixation. The treatment effect was found to be increasing in this order: Jorhat < Katwa < Mohitnagar < Bentlu < Karnal. When the samples were treated with peroxide-CBD-oxalate, the corresponding values were 19.78, 6.35, 29.05, 5.74 and 2.69 mg/g. It indicates the increase in fixation capacity of the samples when compared with the values observed after peroxidation. The results suggest that the coatings of organic matter, free iron oxides and amorphous materials block fixation sites, which are subsequently exposed due to these treatments. The overall treatment effect followed a similar increasing order mentioned above. However, the CBD and oxalate treatment changed the fixation values in this order: Katwa < Jorhat < Bentlu < Karnal < Mohitnagar. The increasing order of fixation in these 5 samples may be explained on the basis of mineralogical make up of these samples. The content of micaceous minerals in the samples (cf. mineralogy) follows the same trend as the K fixation capacity of the cleaned samples. The higher difference between a peroxidized sample and the naturally-occurring clay-organic complex than that observed between a peroxidized sample and cleaned samples suggests that among the materials commonly associated with crystalline components, organic matter has a higher degree of blocking effect in these samples. The relatively higher difference values (3.96, 2.38 and 2.02) in Mohitnagar, Karnal and Bentlu observed with peroxidized and cleaned samples indicate that possibly the mineral -iron oxides/ amorphous materials association is more conspicuous than Katwa and Jorhat samples.

Sl. No.	Soils		K fixed (mg	/ g)	Change in K fixation (mg/g)			
		Untrea Peroxide- Peroxide- P		Peroxidation	Peroxide-	Overall		
		ted	treated	CBD- oxalate		CBD-	treatment	
				treated		oxalate	effect	
						treatment		
		а	b	с	a-b	b-c	a-c	
1.	Bentlu	3.80	17.76	19.78	+13.96	+2.02	+15.98	
2.	Mohitnagar	0.12	2.39	6.35	+2.27	+3.96	+6.23	
3.	Karnal	9.67	26.67	29.05	+17.00	+2.38	+18.38	
4.	Katwa	3.25	5.20	5.74	+1.95	+0.54	+2.49	
5.	Jorhat	0.81	2.11	2.69	+1.39	+0.58	+1.88	
6.	Henningkonglwa	7.67	14.01	21.88	+6.34	+7.87	+14.21	
7.	Palampur	3.00	5.02	13.50	+2.02	+8.48	+10.50	
8.	Naddi	3.28	5.25	14.12	+1.97	+8.87	+10.84	
9.	Chikballapur	12.42	17.65	23.83	+5.23	+6.18	+11.41	
10.	Indore	28.62	36.48	48.96	+7.86	+12.48	+20.34	
11.	Nandyal	20.20	28.56	22.97	+8.36	-5.59	+2.77	
12.	Siraguppa	18.83	26.52	23.83	+7.69	-2.69	+5.0	
13.	Kohima	0.03	0.05	1.48	+0.02	+1.43	+1.54	
14	Tamanda	1.02	1 94	2 33	+0.92	+0.39	+1 31	

Table 10. K-fixation capacity of clay-organic complex with different treatments

Sl. No.	Soils	Los	ss on ignition	(%)	Percentage change in loss on ignition due to			
		Untreate	Peroxide-	Peroxide-	Peroxidatio	CBD- oxalate	Peroxide-	
		d	treated	CBD-	n	treatment	CBD-	
				oxalate			oxalate	
				treated			treatment	
		a	b	с	[a-b/a] *	[b-c/b] * 100	[b-c/a] *	
					100		100	
1.	Bentlu	13.80	10.08	10.16	-27.00	+0.79	+0.58	
2.	Mohitnagar	22.80	14.07	9.00	-38.28	-36.03	-22.23	
3.	Karnal	10.80	6.11	7.60	-43.42	+24.38	+13.79	
4.	Katwa	11.00	8.11	7.49	-26.27	-7.64	-5.63	
5.	Jorhat	14.24	11.32	9.01	-20.50	-20.40	-16.22	
6.	Henningkonglwa	8.92	10.03	6.64	+12.44	-33.79	-38.79	
7.	Palampur	12.20	9.64	9.26	-20.98	-3.94	-3.11	
8.	Naddi	8.71	7.09	8.40	-18.59	-18.47	-15.04	
9.	Chikballapur	15.80	13.59	7.43	-13.98	-45.32	-38.98	
10.	Indore	14.97	11.93	9.36	-20.30	-21.54	-17.16	
11.	Nandyal	8.18	8.04	9.49	-1.71	+18.03	+17.72	
12.	Siraguppa	16.92	12.17	9.04	-28.07	-25.72	-18.49	
13.	Kohima	11.00	10.19	6.84	-7.36	-32.87	-30.45	
14.	Tamanda	8.45	10.48	8.66	+24.02	-17.36	-21.53	

Table 11. Loss on ignition of clay-organic complex with different treatments

The K-fixation capacity values of Alfisols from Henningkonglwa, Palampur, Naddi and Chikballapur were 7.67, 3.00, 3.28 and 12.42 mg/g when no treatment was applied. The values increased up to 14.01, 5.02, 5.25 and 17.65 mg/g in peroxidized samples. The effect of organic matter removal was maximum in Henningkonglwa, followed by Chikballapur, Palampur and Naddi. The fixation increased to 21.88, 13.50, 14.12 and 23.83 mg/g when free iron oxides and amorphous materials were removed from the samples. A close look at the values for the difference (treatment effects) showed that the "difference values" with peroxidized and cleaned samples were more than those with peroxidized and untreated samples, indicating a greater association between clay mineral and iron oxides/amorphous materials leading to blocking of more K fixation sites than is done by OM. The relatively higher "active" iron oxides extracted by acid ammonium oxalate also support this statement. This is expected from these red soils. This observation was, however, just reversed, as observed in Entisols. The clay mineral organic matter association apparently plays a less significant role in blocking K-fixation sites. This, however, seemed quite appreciable in Henningkonglwa and Chikballapur samples. Palampur and Naddi showed almost the same K fixation capacity and had very similar content of mica and mica-vemiculite mixed-layer minerals. The cleaned samples from Henningkonglwa had higher K fixation capacity, though they had a lower mica content. This is explainable based on the high Content of mica-vermiculite interstratified mineral in this sample.

The three black soils were found to have fairly high K-fixation capacity among the 14 soils examined. The Indore soil gave the highest value among the three. This can be explained by the 52% smectite and 31% mica content of this clay. In all three soils, organic matter removal increased K fixation due to surface coating removal and subsequent release of fixing sites for these minerals. However, the values decreased after removing free oxides and amorphous materials except in Indore soil clays. However, the contribution of organic matter was more in the case of Nandyal soils, which may be due to the higher organic matter content of this soil (3.40%) than the other two black soils. The overall effect of H₂O₂, CBD and oxalate treatment was more conspicuous on Indore soils. In Nandyal and Siraguppa, the CBD and oxalate treatments had reduced the fixation values compared to H2O2 treatments.

Like other soils, the Indore sample showed an increasing trend of fixation in both treatments. Nandyal and Siraguppa samples, however, showed a decrease in fixation values when CBD and oxalate treatment were applied to the peroxidized samples. This might suggest the influence and contribution of amorphous materials towards K-fixation. Synthetic aluminosilica gels were observed to fix K⁺ in varying amounts against replacement by common alkali and alkaline earth cations (Van Reeuwijk and de Villiers 1968; Raman and Mortland 1969/1970). The gels showed a marked increase in K-fixing capacity on drying before K saturation. The relative contribution of the exposed (due to the treatment of CBD-oxalate) fixing sites of crystalline components was appeared to be less than that of amorphous materials. This explains the decrease in fixation values in cleaned samples. The contribution of amorphous materials in K-fixation by other samples seemed to be less, and as a result, the relative contribution of the exposed fixing sites of the crystalline component "masked" the effect of amorphous materials. The greater CBD-oxalate treatment effect over the peroxide-treatment effect in the Indore sample indicates the greater association of mineral components with the iron oxides/allophane, unlike the other two black soils. Indore sample's higher "active" iron oxides also support this statement.

In the Ultisols (Kohima and Tamanda), the untreated samples had K-fixation capacities of 0.03 and 1.02 mg/g, respectively. The values increased to 0.05 and 1 .94 mg/g after removing organic matter. The treatment effect was more in the case of the Tamanda sample. The cleaned clay fixed 1.48 and 2.33 mg/g of potassium. According to the abovementioned logic, the CBD-oxalate treatment effect was greater in Kohima than in Tamanda samples, indicating a greater clay mineral-iron oxides/allophane association. In the complexes isolated from the Ultisols, the K fixation was generally very low compared to other soils except for Jorhat and Mohitnagar. Considering the clay mineral composition of these (Ultisols) samples, fixation values were rather low. On removing organic matter and iron oxides/allophanes, the fixation values showed no appreciable increase commensurate with their clay mineral composition. Therefore, the treatments did not appear effective enough to remove blockades from the fixation sites. An examination of the fixation capacity (0.12 mg/g) after peroxide-CBD-oxalate treatment, blockade of exchange sites was appreciably removed, and the fixation went up to 6.35 mg/g.

6. <u>Chemical composition of the clay-organic complex with different treatments</u>

(i) <u>Loss on ignition</u>

Loss on ignition (%) values of clay-organic complex with different treatments are given in Table

11.

Sl. No.	Soils	Los	ss on ignition	(%)	Percentage	Percentage change in loss on ignition due to			
		Untreate	Peroxide-	Peroxide-	Peroxidatio	CBD- oxalate	Peroxide-		
		d	treated	CBD-	n	treatment	CBD-		
				oxalate			oxalate		
				treated			treatment		
		а	b	c	[a-b/a] *	[b-c/b] * 100	[b-c/a] *		
					100		100		
1.	Bentlu	13.80	10.08	10.16	-27.00	+0.79	+0.58		
2.	Mohitnagar	22.80	14.07	9.00	-38.28	-36.03	-22.23		
3.	Karnal	10.80	6.11	7.60	-43.42	+24.38	+13.79		
4.	Katwa	11.00	8.11	7.49	-26.27	-7.64	-5.63		
5.	Jorhat	14.24	11.32	9.01	-20.50	-20.40	-16.22		
6.	Henningkonglwa	8.92	10.03	6.64	+12.44	-33.79	-38.79		
7.	Palampur	12.20	9.64	9.26	-20.98	-3.94	-3.11		
8.	Naddi	8.71	7.09	8.40	-18.59	-18.47	-15.04		
9.	Chikballapur	15.80	13.59	7.43	-13.98	-45.32	-38.98		
10.	Indore	14.97	11.93	9.36	-20.30	-21.54	-17.16		
11.	Nandyal	8.18	8.04	9.49	-1.71	+18.03	+17.72		
12.	Siraguppa	16.92	12.17	9.04	-28.07	-25.72	-18.49		
13.	Kohima	11.00	10.19	6.84	-7.36	-32.87	-30.45		
14.	Tamanda	8.45	10.48	8.66	+24.02	-17.36	-21.53		

Table 11. Loss on ignition of clay-organic complex with different treatments

Five Entisols from Bentlu, Mohitnagar, Karnal, Katwa and Jorhat registered the values of loss on ignition 13.80, 22.80, 10.80, 11.00 and 14.24% in untreated samples; after organic matter removal, the values decreased in all the cases. These values were 10.08, 14.07, 6.11, 8.11 and 11.32% respectively. The value for the Mohitnagar sample sharply reduced to 9.00% after peroxide-CBD-oxalate treatment; for Karnal and Jorhat samples, the removal of organic matter, iron oxides and amorphous materials resulted in a decrease in loss on ignition values to 7.60% and 9.01% while in Bentlu and Katwa samples the values increased to 10.16 and 7.49%.

In Alfisols from Henningkonglwa, Palampur, Naddi and Chikballapur, the loss on ignition values were 8.92, 12.20, 8.71 and 15.80%, respectively, in the samples without treatment; on organic matter removal the samples were found to have a lower loss on ignition. In the case of Palampur, the loss was 9.64% in Naddi, 7.09% and in Chikballapur, 13.59%, while the Henningkonglwa sample registered still higher loss of 10.03%. The loss on ignition further decreased to 6.64% (Henningkonglwa), 9.26% (Palampur), and 7.43% (Chikballapur) when peroxide-CBD-oxalate treatments were given. For the Naddi sample, the loss was 8.40%.

Among the three black soil samples, the Nandyal sample had a minimum loss on ignition value of 8.18%, and Indore and Siraguppa had 14.97 and 16.92%, respectively. The values decreased to 11.93 and 12.17% on peroxide treatment for the last two samples and 9.36 and 9.04% after peroxide-CBD-oxalate treatments. For the Nandyal sample, the values decreased to 9.04% for peroxide treatment and 9.49% for peroxide-CBD-oxalate treatments.

In the case of two Ultisol samples from Kohima and Tamanda (Orissa), the loss on ignition values of 11.00 and 8.45% in untreated samples increased to 10.48% in the Tamanda sample. It decreased to 10.19% when the samples were cleaned of organic matter. However, both samples showed decreased values of 8.66% and 6.84% when organic matter, free iron oxides and amorphous materials were removed.

(ii) Silica

Table 12 gives total SiO_2 (%) of clay-organic complex with different treatments.

Sl. No.	Soils		SiO ₂ (%)		Percentage change in SiO ₂ due to			
		Untreate	Peroxide-	Peroxide-	Peroxidatio	CBD- oxalate	Peroxide-	
		d	treated	CBD-	n	treatment	CBD-	
				oxalate			oxalate	
				treated			treatment	
		а	b	c	[a-b/a] *	[b-c/b] * 100	[b-c/a] *	
					100		100	
1.	Bentlu	50.20	48.49	54.08	+3.40	+11.55	+11.15	
2.	Mohitnagar	36.59	46.29	44.35	+26.50	-4.37	-5.30	
3.	Karnal	8.30	49.91	53.40	+3.33	+6.99	+7.22	
4.	Katwa	46.03	48.59	51.51	+5.56	+6.01	+6.34	
5.	Jorhat	44.73	49.65	55.92	+10.99	+12.63	+14.02	
6.	Henningkonglwa	47.15	49.95	53.07	+5.94	+6.24	+6.62	
7.	Palampur	41.90	44.21	44.52	+5.51	+0.70	+0.74	
8.	Naddi	56.06	48.51	49.20	-15.56	+1.42	+1.23	
9.	Chikballapur	36.56	37.07	46.62	+1.39	+25.76	+26.12	
10.	Indore	44.79	49.72	54.65	+11.00	+9.91	+11.23	
11.	Nandyal	54.42	60.55	54.54	+11.26	-9.92	-11.04	
12.	Siraguppa	42.89	50.13	54.62	+16.88	+8.95	+10.46	
13.	Kohima	43.70	52.54	56.84	+20.23	+8.19	+9.84	
14.	Tamanda	45.10	49.37	51.57	+9.46	+4.45	+4.87	

Table 12. Total silica content of clay-organic complex with different treatments

Bentlu, Mohitnagar, Karnal, Katwa and Jorhat (all Entisols) samples registered the total silica values of 50.20, 36.59, 48.30, 46.03 and 44.73% respectively when no treatment was given. In the case of Mohitnagar, Karnal, Jorhat and Katwa samples, peroxide treatment resulted in an increase in total silica content; the values are 46.29, 49.91, 49.65 and 48.59%, respectively, while in the case of Bentlu samples the same treatment resulted in a decrease of Si0₂, percentage to 48.49, Bentlu, Karnal, Katwa and Jorhat samples have increased values of total silica when the clay-organic complex was finally cleaned from organic matter, free iron oxide and amorphous materials, these values are 54.08, 53.40, 51.51 and 55.92%. The same treatment decreased the total silica value for the Mohitnagar sample; this value (44.35%) is, however, more than that obtained in the sample without treatment.

Henningkonglwa (Nagaland), Palampur, Naddi and Chikballapur (all are Alfisols) samples had 47.15, 41.90, 56.06 and 36.56% of silica. Except for the Naddi samples, the other three samples registered decreasing values when peroxide treatment was given to these samples. For the Naddi sample, the value was 48.51%; in Henningkonglwa, Palampur, and Chikballapur, silica content was 49.95, 44.21 and 37.07%, respectively. In samples obtained from Henningkonglwa and Chikballapur, an inconspicuous increase in SiO₂ percentage was observed when organic matter, free iron oxides and amorphous material were removed. It indicates that the residual crystalline materials have a higher rate of SiO_2 than the amorphous material removed. The same treatment resulted in higher SiO_2 percentage in Palampur (44.52), and Naddi (49.20). Still, the increase was relatively less, thus indicating that the removed amorphous material was less siliceous than in the other two samples of this soil group. Silica content in the aggregate of Vertisols ranged from 42.89-54.42% when no treatment was given, with the maximum value associated with Nandyal and the minimum with Siraguppa. For the Nandyal sample, the value increased to 60.55% when organic matter was removed, but decreased again to 54.54% after peroxide-CBD-oxalate treatment. The decrease in Si0₂ content in peroxide-CBD-oxalate-treated samples indicates that the amorphous material that the CBD-oxalate treatment has removed has a higher $Si0_2\%$ than the remaining crystalline portion. Indore and Siraguppa samples' total silica decreased to 49.72 and 50.13% on peroxide treatment when the organic matter was removed. This indicates that some silica was possibly removed during H202 treatment in this sample. Removal of iron oxide and amorphous material resulted in an overall increase in silica content to 54.65 and 54.62%, respectively. Thus, these two samples behave quite differently from the other Vertisol samples. In these two samples, the removed amorphous materials are less siliceous than the residual crystalline material.

Two Ultisol samples from Kohima and Tamanda (Orissa) registered values of 43.70 and 45.10% when no treatment was given ; peroxide-treated samples gave increased values of 52.54 and 49.37%, while the peroxide-CBD-oxalate treatment resulted in still higher values of 56.84 and 51.57% respectively. Peroxide treatment is supposed to remove organic matter from the aggregates; therefore, after this treatment, the percentage of SiO_2 in all samples should increase as organic matter does not

contain silica. However, in some samples, the results reveal that there have been decreases in the percentage of SiO_2 content. This is possible only if some silica goes out with the peroxide dissolution of organic matter. Earlier work carried out in this laboratory revealed that some silica and other constituents are removed during the peroxidation of organic matter. In samples where this treatment removed free colloidal silica, the residue showed a lower percentage of SiO_2 . On CBD-oxalate treatment, the SiO2 percentage decreased in some samples and increased in others. Whether it would increase or decrease is determined by the composition of the material removed by the treatment. In cases where the material removed has a higher percentage of SiO_2 than the residual crystalline material, the per cent SiO_2 will decrease and vice-versa.

(iii) <u>Sesquioxides</u>

Total sesquioxides (%) of the clay-organic complex with different treatments are shown in table 13.

The Entisol samples from Bentlu, Mohitnagar, Karnal, Katwa and Jorhat contained 29.38, 27.34, 28.18, 27.95 and 29.10% of R_2O_3 , respectively. Organic matter removal resulted in both a decrease and an increase in R_2O_3 content. In Mohitnagar and Katwa samples, R_2O_3 content decreased to 27.10 and 28.98%, while in Bentlu, Karnal and Jorhat samples, the values increased to 30.37, 31.35 and 29.87% respectively. The value decreased in all the cases when peroxide-CBD-oxalate treatment was given •

In the Alfisols from Henningkonglwa (Nagaland) Palampur, Naddi and Chikballapur 30.91, 29.82, 29.73 and 33. 78% are the values for total sesquioxides in samples without treatment. The value increased appreciably in Chikballapur (37.77%) samples when organic matter was removed, for Henningkonglwa and Palampur also, the value increased to 31.85 and 38.81%; Naddi samples, however, suffered a decrease in the sesquioxides content (27.82%) when peroxide treatment was given. Therefore, it appears that in Naddi sample appreciable sesquioxide was complexed with organic matter and removed on peroxide treatment. While comparing the values obtained in the cleaned sample with the peroxide-treated samples, it was observed that the removal of organic matter as well as free iron oxides and amorphous materials resulted in a decrease in sesquioxides content in all the samples; the corresponding values in cleaned samples are 28.41, 27.47, 27.28 and 35.77% respectively. This result agrees with the expectation because the CBD-oxalate treatment largely removed the sesquioxide coating from surfaces and edges of the crystalline minerals.

Sl. No.	Soils		R ₂ O ₃ (%)		Percentage change in R ₂ O ₃ due to			
		Untreate	Peroxide-	Peroxide-	Peroxidatio	CBD- oxalate	Peroxide-	
		d	treated	CBD-	n	treatment	CBD-	
				oxalate			oxalate	
				treated			treatment	
		а	b	с	[a-b/a] *	[b-c/b] * 100	[b-c/a] *	
					100		100	
1.	Bentlu	29.38	30.37	29.64	+3.36	-2.07	-2.49	
2.	Mohitnagar	27.34	27.10	26.42	-0.87	-2.14	-2.13	
3.	Karnal	28.18	31.35	29.47	+11.25	-5.99	-6.67	
4.	Katwa	27.95	28.98	27.16	+3.68	-6.28	-6.51	
5.	Jorhat	29.10	29.87	26.39	+2.64	-11.65	-11.96	
6.	Henningkonglwa	30.91	31.85	28.41	+3.04	-10.80	-11.12	
7.	Palampur	29.82	38.81	27.47	+30.14	-29.22	-38.02	
8.	Naddi	29.73	27.82	27.28	-6.42	-1.94	-1.82	
9.	Chikballapur	33.78	37.77	35.77	+11.81	-5.29	-5.92	
10.	Indore	26.55	25.93	25.23	-2.33	-2.31	-2.26	
11.	Nandyal	26.81	26.38	25.60	-1.60	-2.95	-2.90	
12.	Siraguppa	25.10	26.82	26.08	+6.85	-2.76	-2.95	
13.	Kohima	28.37	32.28	25.12	+13.78	-22.18	-25.23	
14.	Tamanda	27.68	28.88	25.65	+4.33	-11.18	-11.66	

Table 13. Total sesquioxides content of clay-organic complex with different treatments

Sl. No.	Soils		Fe ₂ O ₃ (%)		Percentage change in Fe ₂ O ₃ due to			
		Untreate	Peroxide-	Peroxide-	Peroxidatio	CBD- oxalate	Peroxide-	
		d	treated	CBD-	n	treatment	CBD-	
				oxalate			oxalate	
				treated			treatment	
		a	b	с	[a-b/a] *	[b-c/b] * 100	[b-c/a] *	
					100		100	
1.	Bentlu	10.95	10.95	10.25	0	-6.39	-6.39	
2.	Mohitnagar	10.94	9.10	9.10	-16.89	0	0	
3.	Karnal	11.97	10.43	8.94	-12.86	-12.45	-14.28	
4.	Katwa	12.57	12.09	8.72	-3.82	-26.81	-27.87	
5.	Jorhat	11.12	10.87	5.25	-2.25	-51.70	-50.54	
6.	Henningkonglwa	12.50	12.37	6.21	-1.04	-49.30	-49.79	
7.	Palampur	11.39	11.39	6.23	0	-45.30	45.30	
8.	Naddi	11.50	9.71	8.91	-1.55	-6.95	-8.24	
9.	Chikballapur	14.30	14.30	11.57	0	-19.09	-19.09	
10.	Indore	9.81	9.75	9.51	-0.61	-2.46	-2.44	
11.	Nandyal	10.00	10.00	8.93	0	-10.70	-10.70	
12.	Siraguppa	8.33	8.11	7.57	-2.64	-6.65	-6.48	
13.	Kohima	11.39	11.39	3.99	0	-67.97	-64.97	
14.	Tamanda	9.77	9.77	3.61	0	-63.05	-63.05	

Table 14. Total Fe₂O₃ content of clay-organic complex with different treatments

Indore and Nandyal samples had similar sesquioxide content of 26.55 and 26.81%, while in Siraguppa, it was 25.10% in the clay-organic complex. The values slightly decreased when organic matter was removed from Indore (25.93%) and Nandyal samples (26.38%), but in the Siraguppa sample, it increased only slightly to 26.82%. The cleaned (free from organic matter, iron oxides and amorphous materials) sample from Siraguppa had less R_2O_3 per cent than what was observed in peroxide-treated samples, while in the case of Nandyal and Indore cleaned samples resulted in a slight decrease in R_2O_3 value of 25.60 and 25.23 respectively.

Two Ultisol samples of Kohima and Tamanda (Orissa) had 28.37% and 27.68% of total sesquioxide content. Kohima samples registered an increased amount of R_2O_3 (32.28%) when organic matter was removed, while in Tamanda, the increase was only slight (28.88%). Removal of organic matter, free iron oxides and amorphous materials resulted in an overall decrease in sesquioxide content; these values are 25.12 and 25.65%. This is similar to what was observed in Alfisols.

(iii) $\underline{\text{Total Fe}_2O_3}$

Table 14 gives the total Fe_2O_3 (%) of the untreated and treated clay-organic complex. Entisols from Bentlu, Mohitnagar, Karnal, Katwa and Jorhat had more or less similar values of Fe_2O_3 . These values were 10.95, 10.94, 11.97, 12.57 and 11.12% respectively. The values decreased slightly when organic matter was removed from the samples except in the Bentlu sample, which registered no change in the value; the values for other samples were 9.10, 10.43, 12.09 and 10.87%, respectively. Peroxide-CBD-oxalate treatment resulted in slight or no change in Fe_2O_3 content for Bentlu and Mohitnagar samples. At the same time, it caused a decrease in the Fe_2O_3 content (8.94, 8.72 and 5.25%) for Karnal, Katwa and Jorhat samples.

Total Fe₂O₃ content in Henningkonglwa, Palampur, Naddi and Chikballapur (all Alfisols) were 12.50, 11.39, 11.50 and 14.30% respectively for samples without any treatment. Out of 4 Alfisols, two (Palampur and Chikballapur) registered the same values (11.39 and 14.30), and the other two (Henningkonglwa and Naddi) had lower values (12.37 and 9.71) in peroxide-treated samples than that observed in samples having no chemical treatment. The peroxide-CBD-oxalate treatment reduced the iron content in all these samples. The values were 6.21, 6.23, 8.91 and 11.57% in Henningkonglwa, Palampur, Naddi and Chikballapur, respectively. In untreated samples from Indore, Siraguppa and Nandyal (black soils), the total Fe2O3 values were 9.81, 8.33, and 10.00%, respectively. For Siraguppa, the value decreased to 8.11% in the peroxide-treated sample; the same treatment resulted in a slightly low value (9.75%) for the Indore sample, while the Nandyal sample showed no change in the total iron oxide value (10.00%). The removal of organic matter, iron oxide, and amorphous material decreased Fe₂O₃ value, viz. 9.51, 7.57 and 8.93% for Indore, Siraguppa and Nandyal samples, respectively.

When no treatment was given, the two Ultisol samples from Kohima and Tamanda (Orissa) contained 11.39 and 9.77% of total iron oxides. Removal of organic matter resulted in no change in these values, showing virtually no variation and little association of Fe with organic matter. The values were reduced drastically to 3.99 and 3.61% when the peroxide-treated samples were given CBD and oxalate treatment, thereby indicating that a lot of iron was associated with CBD and oxalate extractable material.

Removal of organic matter reduced the Fe_2O_3 content in 8 samples to 0.6 to 16.9% (Table 14), indicating that Fe in varying quantities were removed with the removal of organic matter. The reduction was highest in two Entisols viz. Mohitnagar and Karnal are the lowest in Vertisol (Indore). In these samples, the complex formation of Fe- with organic matter is unquestionable. In six samples, organic matter removal did not bring about any significant change in Fe_2O_3 content. Ultisols, some Alfisols, and one of Entisol and Vertisol samples showed this behaviour. This suggests that organic matter possibly does not form separate complexes with Fe_2O_3 but some adsorption complex on precipitated iron oxide, which do not get solubilized on peroxide treatment. CBD-oxalate treatment led to a high percentage reduction in Fe_2O_3 in Uitisols, some Alfisols and one Entisol samples (Table 14). Few samples did not show any significant change; some Alfisols, Vertisols and few Entisols suffered a relatively low percentage reduction in Fe_2O_3 content. (v) Total Al₂O₃

The total Al₂O₃ of untreated and treated clay-organic complexes are given in table 15.

Out of five Entisols samples, Mohitnagar and Katwa had similar alumina content (16.43 and 15.38%, respectively), while those from Bentlu, Karnal and Jorhat registered more or less similar values (18.43, 17.01 and 17.98% respectively) when no treatment was qiven. Organic matter removal increased the values. The corresponding values were 18.00, 16.89, 19.22, 20.92 and 18.00% respectively for Mohitnagar, Katwa, Bentlu, Karnal and Jorhat. The removal of organic matter, iron oxides and amorphous materials resulted in a further increase in alumina content in all but one sample. In the case of Bentlu (19.39%) and Jorhat (21.14%), samples registered higher values, whereas in the case of Mohitnagar and Karnal Al₂O₃ content decreased to 17.32% and 20.53% respectively.

CI No	Saila	$A I \cdot O \cdot (\theta/)$			Percentage change in AlaOa due to			
51. INO.	Solis		AL2O3 (%)		Perce	ntage change inAl ₂ O ₃ d	iue to	
		Untreated	Peroxide-	Peroxide-	Peroxidation	CBD- oxalate	Peroxide-	
			treated	CBD-		treatment	CBD-	
				oxalate			oxalate	
				treated			treatment	
		а	b	с	[a-b/a] * 100	[b-c/b] * 100	[b-c/a] *	
							100	
1.	Bentlu	18.43	19.22	19.39	+4.28	+0.88	+0.90	
2.	Mohitnagar	16.43	18.00	17.32	+9.55	-3.77	-4.13	
3.	Karnal	17.01	20.92	20.53	+22.98	-1.86	-2.29	
4.	Katwa	15.38	16.89	18.44	+9.82	+9.17	+10.07	
5.	Jorhat	17.98	18.00	21.14	+0.11	+17.44	+17.46	
6.	Henningkonglwa	18.41	19.48	22.20	+5.81	+13.96	+14.77	
7.	Palampur	18.43	27.42	21.24	+48.70	-22.50	-33.53	
8.	Naddi	18.23	18.11	22.37	-5.23	+23.52	+23.36	
9.	Chikballapur	19.48	23.47	24.20	+20.48	+3.11	+3.70	
10.	Indore	16.74	16.18	15.72	-3.34	-2.72	-2.70	
11.	Nandyal	16.81	16.38	16.63	-2.55	+1.52	+1.24	
12.	Siraguppa	16.77	18.71	18.51	+11.56	-1.07	-1.13	
13.	Kohima	17.48	20.89	21.13	+19.50	+1.15	+1.37	
14.	Tamanda	17.91	19.11	22.04	+6.90	+15.30	+16.30	

Table 15. Total Al₂O₃ content of clay-organic complex with different treatments

In Alfisols of Henningkonglwa, Palampur, Naddi, and Chikballapur, untreated samples of total alumina content were 18.41, 18.43, 18.23 and 19.48%, respectively. When treated with peroxide appreciable increase was observed in the Palampur (27.42%) and Chikballapur (23.47%) samples, a slight increase in the Henningkonglwa (19.48%) sample and a slight decrease in Naddi (18.11%) sample. The corresponding values were 22.20, 21.24, 22.37 and 24.20% when the samples were treated with peroxide-CBD-oxalate. The overall increase in Al₂O₃ percentage after removing organic matter and amorphous material was observed in the Henningkonglwa, Chikballapur, and Naddi samples. This signifies that the materials removed by the treatments have a relatively lower proportion of aluminium, and therefore Al₂O₃ percentage in the residual material was increased.

In untreated clay-organic complex, all three Vertisols had similar Al_2O_3 content; the values were 16.74, 16.77 and 16.81% for Indore, Siraguppa and Nandyal samples, respectively. The values increased to 18.71% in the Siraguppa sample on organic matter removal, while in the Indore and Nandyal samples, values went down to 16.18 and 16.34% in the Nandyal sample. Al_2O_3 content increased to 16.63% in the Nandyal sample when peroxide-CBD-oxalate treatment was given. The same treatment resulted in 15.72 and 18.51% Al_2O_3 , respectively, for Indore and Siraguppa samples. The three Vertisols behave quite differently. An increase in Al_2O_3 and content on peroxidation in the Siraguppa sample indicates that little or no Al_2O_3 was removed with organic matter removal. Some aluminium was removed on peroxidation in Nandyal and Indore samples.

Kohima and Tamanda (Orissa), the two Ultisol samples registered 17.48 and 17.91% Al₂O₃ in untreated samples. Both these samples, after removing organic matter, were found to have increased amounts of alumina (20.89 and 19.11%, respectively)• The values further increased to 21.13 and 22.04%, respectively, when peroxide-CBD–oxalate treatments were given to remove organic matter, free iron oxides and amorphous materials. The Ultisol samples also behaved similarly to the Alfisol samples.

(vi) CaO

Table 16 gives the CaO (%) content of the clay-organic complex and the change in content due to different treatments.

Sl. No.	Soils	CaO (%)			Percentage change in CaO due to			
		Untreate	Peroxide-	Peroxide-	Peroxidatio	CBD- oxalate	Peroxide-	
		d	treated	CBD-	n	treatment	CBD-	
				oxalate			oxalate	
				treated			treatment	
		а	b	c	[a-b/a] *	[b-c/b] * 100	[b-c/a] *	
					100		100	
1.	Bentlu	5.69	5.69	3.62	0	36.37	36.37	
2.	Mohitnagar	6.85	6.85	4.79	0	30.07	30.07	
3.	Karnal	6.60	6.60	4.62	0	15.15	15.15	
4.	Katwa	7.41	5.54	5.54	25.23	0	0	
5.	Jorhat	8.69	8.69	6.17	0	28.99	28.99	
6.	Henningkonglwa	9.65	6.62	5.69	31.40	14.05	9.63	
7.	Palampur	11.20	2.39	1.76	78.66	26.36	5.62	
8.	Naddi	8.78	7.81	4.06	11.04	48.01	42.71	
9.	Chikballapur	8.55	8.01	4.38	6.301	45.32	42.45	
10.	Indore	9.22	8.74	5.05	5.20	42.22	40.02	
11.	Nandyal	10.12	6.35	5.38	37.25	15.27	9.58	
12.	Siraguppa	10.25	8.23	6.68	19.70	18.83	15.12	
13.	Kohima	7.70	5.69	5.69	12.98	0	0	
14.	Tamanda	9.11	5.75	5.75	10.97	0	0	

 Table 16. Total CaO content of clay-organic complex with different treatments

Entisols from Bentlu, Mohitnagar, Karnal, Katwa and Jorhat had 5.69, 6.85, 6.60, 7.41 and 8.69% CaO respectively in the untreated clay-organic complex. The value of CaO was 6.85% for Mohitnagar when organic matter was removed from the sample; the value was observed in the Katwa sample as 5.54%; the value remained the same (8.69%) in the case of the Jorhat sample, while in Bentlu and Karnal samples CaO content did not change. Bentlu and Karnal samples showed 3.62 and 4.62% CaO content when peroxide-CBD-oxalate treatment was given; CaO content remained the same as 5.54% (Katwa) due to the same treatment. CaO content decreased again to 6.17% in the Jorhat sample and to 4.79% in Mohitnagar samples.

In the particle size separation for mineralogical analysis, the soil is pretreated either with HCl or NaOAc solution of pH 4.5 and then by CBD. Elemental analysis of clay separated after giving such pretreatments for the soil groups studied rarely gives a value of more than 1% CaO content. However, the residues from the naturally occurring clay-organic complex (particle size $0.05-2 \mu$) after removal of organic matter and amorphous material contained fairly high CaO. This indicates that highly insoluble Ca-minerals like apatites, carbonates, and feldspars are constituents of these complexes in various proportions. However, the total content of any of these mineral constituents is low; therefore, attempts to identify them by X-ray diffraction were unsuccessful. It is obvious that in the routine clay separation procedures, such minerals are dissolved by the acid treatment normally used for removing carbonates; ca-feldspars, however, survive and contribute to the Ca-content of the cleaned clays.

Four Alfisols Henningkonglwa and Naddi had similar CaO content of 9.65 and 8.78% respectively; Palampur and chikballapur samples contained 11.20 and 8.55% in untreated conditions. Removal of organic matter resulted in a drastic reduction of CaO value in the Palampur sample (2.39%). Besides, peroxide treatment resulted in a decrease in CaO content in Naddi (7.81%), Henningkonglwa (6.62%) and chikballapur (8.01%). When the samples were made free from organic matter, free iron oxides and amorphous materials, CaO content decreased in all these samples. The values came down to 5.69% (Henningkonglwa), Naddi (4.06%), Palampur (1.76%) and Chikballapur (4.38%). It, therefore, appears that in the Palampur sample, much of the Ca was associated with organic matter and was removed with its removal, whereas in other samples, a relatively lower proportion of Ca was associated with organic matter. The results also indicate that part of the Ca is also associated with amorphous material. Ca in these fractions possibly plays the role of a binding cation, whereas in the residue, Ca may remain as phosphates and carbonates, possibly more as Ca feldspars.

Among the three black soil samples, Siraguppa and Nandyal had relatively higher values of 10.25 and 10.12%, while in Indore, the value was 9.22% in the untreated clay-organic complex. Peroxide treatment resulted in a decrease of CaO value to 8.23% in the Siraguppa sample; the same treatment resulted in a slight reduction in the Indore sample (8.74%), while in the Nandyal sample, a

decrease in CaO content (6.35%) was very high. Peroxide-CBD-oxalate treatment drastically reduced CaO content in all three black soil samples; the corresponding values were 5.05, 6.68 and 5.38% in Indore, Siraquppa and Nandyal samples. The content of CaO in the treated samples suggests that the aggregates contain Ca-bearing primary minerals.

In the case of two Ultisols from Kohima and Tamanda, untreated samples contained 7.70 and 9.11% of CaO. Organic matter removal resulted in an appreciable decrease in both Kohima (5.69%) and Tamanda (5.75%) samples. Peroxide-CBD-oxalate treatments resulted in no change in CaO values in both the samples.

(vii) MgO

The MgO content of the clay-organic complex and its change due to peroxide and CBD-oxalate treatment has been presented in Table 17.

Sl. No.	Soils	MgO (%)			Percentage change in MgO due to			
		Untreate d	Peroxide- treated	Peroxide- CBD- oxalate treated	Peroxidatio n	CBD- oxalate treatment	Peroxide- CBD- oxalate treatment	
		а	b	c	[a-b/a] * 100	[b-c/b] * 100	[b-c/a] * 100	
1.	Bentlu	1.10	1.60	1.09	+45.45	-31.87	-46.45	
2.	Mohitnagar	3.10	2.44	2.05	-21.29	-15.98	-12.58	
3.	Karnal	3.10	2.09	1.20	-32.58	-42.58	-28.71	
4.	Katwa	2.67	2.80	1.43	+4.86	-48.93	-51.31	
5.	Jorhat	1.76	2.02	0.43	+14.77	-78.71	-90.34	
6.	Henningkonglwa	2.00	0.92	0.23	-54.00	-75.00	-34.50	
7.	Palampur	2.80	1.66	1.59	-40.71	-4.21	2.50	
8.	Naddi	2.02	1.85	0.30	-8.41	-83.78	-76.73	
9.	Chikballapur	1.65	1.58	0.39	-4.24	-75.31	-72.12	
10.	Indore	2.59	2.04	0.84	-26.96	-76.47	-60.23	
11.	Nandyal	0.49	0.17	0.15	-65.30	-11.76	-4.08	
12.	Siraguppa	2.20	2.11	0.74	-4.09	-64.92	-80.45	
13.	Kohima	1.60	1.00	0.57	-37.50	-43.00	-26.87	
14.	Tamanda	1.26	0.99	0.47	-21.42	-52.52	-41.27	

Table 17. Total MgO content of clay-organic complex with different treatments

Entisols from Bentlu, Mohitnagar, Karnal, Katwa and Jorhat contained 1.10, 3.10, 3.10, 2.67 and 1.76% of MgO, respectively when no treatment was given. When organic matter was removed, the MgO content was reduced to 2.44 and 2.09% in the Mohitnagar and Karnal samples, while the reverse happened in the Bentlu, Katwa and Jorhat samples. The corresponding values were 1.60, 2.80 and 2.02%. Removal of organic matter, free iron oxides and amorphous materials reduced the MgO content to 1.09, 2.05, 1.20 and 1.43 in Bentlu, Mohitnagar, Karnal and Katwa samples, respectively. In Jorhat samples the value obtained was 0.43%.

Henningkonglwa, Palampur, Naddi, and Chikballapur samples (all Alfisols) contained 2.00, 2.80, 2.02 and 1.65% of MgO in the naturally- occurring clay-organic complex. The values decreased when peroxide treatment was given. MgO content was observed to be 0.92, 1.66, 1.85, and 1.58% for Henningkonglwa, Palampur, Naddi, and Chikballapur, respectively. The values decreased to 0.23, 1.59, 0.30 and 0.39%, respectively, when peroxide-CBD-oxalate treatment was given.

Out of three black soils, Indore samples had a maximum of 2.59% MgO, followed by Siraguppa (2.20%) and Nandyal (0.49%) when no treatment was given. Organic matter removal resulted in decrease in MgO content. The values were 2.04, 2.11 and 0.17% for Indore, Siraguppa and Nandyal samples, respectively. Removal of iron oxides and amorphous materials along with organic matter further decreased MgO content to 0.84, 0.74 and 0.15% in those three samples.

In untreated, Kohima and Tamanda (Ultisols) samples had 1.60 and 1.26% MgO; organic matter removal decreased MaO content to 1.00 and 0.99%. On removal of organic matter, free iron oxides and amorphous materials, MgO content was further reduced to 0.57 and 0.47%.

MgO content in the cleaned clay was rather low. Three of the Entisols and an Alfisol sample showed more than 1% MgO content, possibly due to chlorite in these samples. The Vertisol clays have a rather low content of MgO (0.15-0.84%), considering their smectite-dominant nature. The smectite in these samples, therefore, appears to be beidellite. Khandekar (1980) reported 52% and 70% of Beidellite in Indore and Siraguppa soil clays, respectively. Notably, a large portion of the Mg remains associated with organic matter and amorphous material. The role of Mg as a binding cation in the formation of clay-organic complex is thus indicated.

(viii) K₂0

The K₂O content in the clay-organic complex and its variation in the removal of organic matter and amorphous materials in succession has been presented in Table 18.

Sl. No.	Soils	K2O (%)			Percentage change in K ₂ O due to			
		Untreate	Peroxide-	Peroxide-	Peroxidatio	CBD- oxalate	Peroxide-	
		d	treated	CBD-	n	treatment	CBD-	
				oxalate			oxalate	
				treated			treatment	
		a	b	с	[a-b/a] *	[b-c/b] * 100	[b-c/a] *	
					100		100	
1.	Bentlu	2.71	2.94	3.06	+8.49	+4.05	+4.42	
2.	Mohitnagar	2.90	2.92	4.94	+0.69	+69.17	+69.45	
3.	Karnal	3.80	4.46	4.16	+17.36	-6.72	-7.89	
4.	Katwa	5.70	3.03	2.30	-46.76	-24.09	-12.80	
5.	Jorhat	2.12	2.30	2.60	+8.49	+13.04	+14.15	
6.	Henningkonglwa	3.13	3.13	3.70	0	+18.21	+18.21	
7.	Palampur	2.71	3.47	3.21	+28.04	-7.49	-9.59	
8.	Naddi	4.26	5.10	4.13	+17.37	-19.01	-22.53	
9.	Chikballapur	1.11	2.01	1.26	+81.08	-37.31	-67.56	
10.	Indore	1.92	2.06	1.85	+7.29	-10.19	10.93	
11.	Nandyal	1.14	1.35	1.02	+18.42	-24.44	-28.94	
12.	Siraguppa	1.02	1.29	1.04	+26.47	-19.37	-24.51	
13.	Kohima	2.56	2.92	3.10	+14.06	+6.16	+7.03	
14.	Tamanda	2.25	2.33	2.44	+3.55	+4.72	+4.88	

Table 18. Total K₂O content of clay-organic complex with different treatments

Bentlu, Mohitnagar, Karnal, Katwa and Jorhat (Entisols) contained 2.71, 2.90, 3.80, 5.70 and 2.13% of total potash when no treatment was given. The content increased to 2.94, 2.92, 4.46 and 2.30% in Bentlu, Mohitnagar, Karnal and Jorhat samples when organic matter was removed. Percentage increase in K_2O in the organic matter-free samples ranged from 0.69 to 17.36. In the Katwa sample, however, the content decreased to 3.03%. K_2O content increased to 3.06, 4.94 and 2.60% in Bentlu, Mohitnagar and Jorhat samples when peroxide-CBD-oxalate treatment was given. The same treatment reduced the values to 4.16 and 2.30% for Karnal and Katwa samples. In the Entisols, it appears that K in the amorphous constituents is variable. In general, the fact that appreciable K is associated with the amorphous constituents in some of the clay-organic complexes points to the occurrence of K-zeolites. However, there is no other evidence to substantiate this contention, as there is no way to isolate the K-zeolites selectively.

Henningkonglwa, Palampur, Naddi and Chikballapur (all Alfisols) were found to have 3.13, 2.71, 4.26 and 1.11%, respectively, when no treatment was given in the clay-organic complex. The removal of organic matter resulted in an increase in K₂O content for Palampur (3.47%), Naddi (5.10%) and Chikballapur (2.01%) with no change in the Henningkonglwa sample. The values decreased after removing free iron oxides and amorphous materials along with organic matter to 3.21%, 4.13% and 1.26% for Palampur, Naddi and Chikballapur samples, while the content of potash increased slightly to 3.70% in Henningkonglwa. Very little to no potassium seems to be associated with amorphous material in these samples. In Henningkonglwa, K content in the amorphous portion is rather low; as a result, its

removal led to an 18.21% increase in the K_2O content of the residue. The decrease in K_2O content the residue in other samples varied from 7.49 to 37.31%.

 K_2O content in untreated samples from Indore, Siraguppa and Nandyal (Vertisols) were found as 1.92, 1.02 and 1.14% respectively. The values increased slightly to 2.06, 1.29 and 1.35% when samples were treated with peroxige. However, the K2O content in the cleaned samples ultimately decreased to 1.85, 1.04 and 1.02% for these samples. The increase in organic matter removal was of the order of 7.29 to 26.47%, but on amorphous matter removal, the drop in K₂O content in the residue was 10.2 to 24.4%. This indicates that much of the K was associated with the amorphous material on the Vertisol clay-organic complex.

Kohima and Tamanda (Orissa) samples were found to contain 2.56 and 2.25% K_2O in untreated conditions; while peroxide treatment increased the values to 2.92 and 2.33%. This meant an increase of 3.55% in Tamanda and 14.06% in Kohima. The peroxide-CBD-oxalate treatment increased the values further to 3.10 and 2.44%, respectively. The K_2O percentage of the residual material increased greatly due to the removal of both organic matter and amorphous material, indicating that in these samples K residues mainly in the crystalline portion of the clay-organic complex.

4.4.7. Content of amorphous constituents- Chemical characterization

The constituents extracted by acid ammonium oxalate were utilised to calculate allophane using Alexiades and Jackson's (1966) method and de Villiers' (1971) method. The former calculation method resulted in higher values, as shown in Table 19. The following discussion is based on the amorphous material calculated by de Villiers' method.

Table 19. Chemical composition of amorphous constituents present in cia	ay-organic
complex	

Sl. No.	Soils	SiO ₂	Al ₂ O ₃	SiO ₂ /Al ₂ O ₃	Fe ₂ O ₃	Allophane (%)	
		%	%	%	%	(1)**	(2)+
1.	Bentlu	0.0147	0.135	0.18	7.365	0.0212	0.1663
2.	Mohitnagar	0.0671	0.580	0.19	1.345	0.0966	0.0719
3.	Karnal	0.0164	0.850	0.03	4.835	0.0236	0.9626
4.	Katwa	0.0222	0.065	0.58	5.025	0.0320	0.0969
5.	Jorhat	0.0151	0.115	0.22	5.025	0.0217	0.1445
6.	Henningkonglwa	0.0241	0.090	0.45	5.300	0.0347	0.1268
7.	Palampur	0.0192	0.095	0.34	3.120	0.0276	0.1268
8.	Naddi	0.0111	0.485	0.04	10.584	0.0160	0.5512
9.	Chikballapur	0.0149	0.120	0.21	6.315	0.0215	0.1500
10.	Indore	0.0099	0.040	0.42	1.875	0.0143	0.0554
11.	Nandyal	0.0163	0.195	0.14	5.421	0.0234	0.2348
12.	Siraguppa	0.0101	0.055	0.31	2.705	0.0145	0.0723
13.	Kohima	0.0263	0.095	0.47	7.033	0.0379	0.1348
14.	Tamanda	0.0182	0.085	0.36	5.713	0.0262	0.1147

(1)** = According to de Villiers (1871)

(2) + = According to Alexiades and Jackson (1966)

The 5 Entisols from Bentlu, Mohitnagar, Karnal, Katwa and Jorhat contained 0.021, 0.014, 0.024, 0.032 and 0.022% of allophane. There was not a distinct relationship between organic matter and allophane; nevertheless, in black and red (Alfisols) soil samples, there was a tendency for higher organic matter content to be associated with lower allophone content. A similar observation was also made when content of allophane were compared with CEC values; it appears that higher CEC values may be due more to the effect of organic matter than allophane. Although not a very clear relationship was observed with allophane and total surface area, still an increasing trend of surface area values due to higher values of allophone were noticed; this is expected considering a very high surface area of allophane even if present in a very small amount in these mica/kaolinite dominated samples. The oxalate-extracted Fe₂O₃ content was 7.365, 5.025, 4.835 and 1.345% in Bentlu, Katwa, Jorhat, Karnal and Mohitnagar samples. No relationship was observed between these iron oxide values and total Fe₂O₃ values. Such was also the observation with organic matter (Table 19).

Out of 4 Alfisols, Henningkonglwa (Nagaland) and Palampur had higher values for allophane in clay-organic complex (0.035 and 0.028% respectively), while Naddi and Chikballapur samples had 0.016 and 0.021%. Relatively higher allophone content may explain the higher CEC values of the Nagaland sample than the Palampur sample. However, the CEC values and the allophane content for Naddi and Chikballapur samples showed no such relation.

The Fe₂O₃ content in the acid-oxalate-extract was maximum in Naddi (10.584%), followed by Chikballapur (6.315%), Henningkonglwa (5.300%) and Palampur (3.122%) (Table19). The extracted Fe₂O₃ is expected to correlate with total Fe₂O₃ positively but no such correlation was observed. It may be due to the fact that the extractability of iron by any one extractant depends on the form and state of iron in these samples. When these Fe₂O₃ values were compared with organic matter content in clayorganic complex, higher organic matter content was associated with lower oxalate-extractable iron, especially in Palampur and Henningkonglwa samples. The allophane contents, however, were found to have a direct relationship with the organic matter content in clay- the organic complex in Henningkonglwa and Palampur samples suggesting a possible allophane-organic association in the complex. Similar observations were reported earlier in the case of black soil samples in this section. Electron microscopic observation lends support to this inference.

Among the three Vertisol samples, the allophane content was the same in Indore and Siraguppa (0.014%); in Nandyal, it was more (0.023%). There was a direct relationship with the organic matter content and the amorphous constituents extracted by acid oxalate, with higher organic matter content associated with higher allophane content. The higher values for the Nandyal sample might explain the relatively higher total surface area in this case. When extracted Fe₂O₃ values were compared, it was observed to be more in the case of the Nandyal (5.421%) sample, followed by Siraguppa (2.705%) and Indore (1.875%). A more or less similar trend was observed in the total Fe₂O₃ content of these soil samples (Table 19).

Two Ultisols from Kohima and Tamanda (Orissa) contained 0.038 and 0.026% of allophane. There was a direct relationship between total surface area, CEC, and organic matter content and the allophane content of the respective sample.

These samples' Oxalate extractable iron oxides were 7.033 and 5.713%, respectively. Total iron oxide content was also higher in the Kohima sample (11. 39%) than in Tamanda (9.77%) and has a direct relationship with organic matter *content* in the clay-organic complex.

It is evident from Table 19 that iron is the major constituent of the Oxalate extractable amorphous material in the clay-organic complex. Comparison between soil groups does not reveal any specific relationship. Highest content of amorphous iron oxide was found in an Alfisol and lowest in an Entisol. In general, Alfisols, Ultisols and Entisols have a fairly high content of this constituent in the Clay-organic complex formed. The next abundant constituent is Al₂O₃, although it occurs in much less quantity. Here again, the distribution does not bear any specific relationship to the soil groups, but relatively higher content in Entisols and Alfisols is indicated. Whether this alumina occurs as free hydrated oxide, in combination with SiO2 (as in allophane), or as both in any one sample is difficult to predict without any suitable technique to distinguish between the two forms. Following de Villiers

(1971), this was considered part of allophane only in this study. Whether it occurs as allophane or as free alumina in the clay-organic complex, it plays a significant role in complex formation with organic matter and as binding material in forming aggregates (cf. electron microscopic studies of the complex). SiO₂ content is rather low. Considering the SiO₂ / Al₂O₃ molar ratios, these allophanes are not comparable to those in volcanic ash soils. Earlier investigation with some samples of the soil groups' studies where extraction was made with Hashimoto and Jackson's method revealed silicious allophane's existence. As indicated in table 4 0.5N NaOH extraction brings out unduly high SiO₂ involving dissolution of fine grained silicate crystals. Therefore, the highly silicious nature of the allophanes in these soils is not a reality. The present study indicates an opposite trend, i.e., higher alumina content in the amorphous constituent, particularly in the complex. Though the amorphous silica content is low, part of it has been found also to occur as free silicic acid in some samples (cf. electron micrograph, etc.); most of it, however, appears as allophane in the clay-organic complex is difficult until different forms of silica can be selectively dissolved. At present, no such method is available. Such methods need to be developed for better quantitative estimation of allophanes.

4.4.8. <u>Infrared absorption characteristics of clay-organic complex and its</u> <u>change due to removal of organic matter, free oxides and allophones</u>

(i) <u>Frequencies between 3500 and 3950 cm⁻¹</u>

According to Farmer and Russell (1964), coupling between the vibrations of the two hydroxyl groupings can give rise to two frequencies of vibration, one in which the two hydroxyl groups are 180° out of phase and the other in-phase vibration. The anti-symmetric (out of phase) is infrared active and is the origin of the strong band at 3675 cm⁻¹. Symmetric vibration is infrared and inactive, but the weak band at 3647 cm⁻¹ could arise from this vibration if the symmetry of the structure is not ideal. An alternative assignment is that it arises from hydroxyl groups shared between aluminium and iron, as the octahedral layer may contain a small proportion of iron. Progressively increasing substitution of aluminium for silicon in the tetrahedral layer of the pyrophyllite structure with the introduction of balancing interlayer cations gives rise to two absorption bands at 3660 and 3627 cm⁻¹ with the lower-frequency band increasing in intensity with increasing aluminium substitution and the higher-frequency component decreasing.

In the Indore black soil sample in coarse fraction (CF) and peroxide-treated coarse fraction (PTCE) all bands in this zone were found as shoulders, which were absent in POTCF (after removal of organic matter, iron oxides and amorphous constituents). In PTCF, a 3760 cm⁻¹ band was missing (Fig.6). In Siraguppa, only one shoulder was found at 3620 cm⁻¹ in CF, while in PTCF and POTCF, the shoulders were common except 3620 cm⁻¹ which was missing in POTCF (Fig. 7). In Nandyal many
shoulders were detected in this zone only in CF (Fig.8). After removing organic matter, iron oxides and amorphous constituents the number of shoulders was, however, found decreasing. The bands above 3700 cm⁻¹ are present only in CF (without treatment).

In Mohitnagar, the bands were common in CF and PTCF except 3590 cm^{-1,} which was absent in CF (Fig.9). In POTCF, only one shoulder at 3650 cm⁻¹ was detected, and this band was common in all three treatments. In Karnal samples, however, the number of shoulders increased as the samples were cleaned from organic matter, iron oxides, and amorphous materials (Fig. 10). Noticeably, one band at 3755 cm⁻¹ was observed in POTCF.

In the Chikballapur samples, quite interesting observations were made, unlike the above five samples (Fig.11). In CF and PTCF, the bands were well delineated and did not have shoulders except in POTCF. The strong CF and PTCF peaks at 3685 and 3680 cm⁻¹ shifted to 3600 in POTCF. A peak (weak) at 3805 was observed when the sample was free from organic matter, iron oxides and amorphous materials.



Figure 6. Infrared spectra of 2-0.05 µ fraction of a Vertisol (Indore)



Figure 7. Infrared spectra of 2-0.05 µ fraction of a Vertisol (Siraguppa)



Figure 8. Infrared spectra of 2-0.05 µ fraction of a Vertisol (Nandyal)



Figure 9. Infrared spectra of 2-0.05 µ fraction of an Entisol (Mohitnagar)



Figure 10. Infrared spectra of 2-0.05 µ fraction of an Entisol (Karnal)



Figure 11. Infrared spectra of 2-0.05 µ fraction of an Alfisol (Chikballapur)

In the Bentlu sample, two very weak bands at 3900 and 3800 cm-1 and one at 3595 were observed in CF, which were missing in PTCF and POTCF. Otherwise, all appeared as shoulder bands in this zone (Fig.12).

For Naddi samples, in CF (without treatment), one peak at 3770 cm⁻¹ was observed, besides all were shoulders in 3685, 3650, 3605, 3585 3555 cm⁻¹ (Fig. 13). The strong peak at 3590 cm⁻¹ in POTCF shifted about 30 cm⁻¹ in PTCF and at 3560 cm⁻¹ it was registered as a strong absorption band. Two peaks at 3920 and 3840 cm⁻¹ and one shoulder at 3800 cm⁻¹ were detected in POTCF, which were otherwise absent in CF and PTCF.

The number of bands in this region decreased from CF to POTCF in Palampur soil. The bands at higher frequency were missing in PTCF, which reappeared (one at still higher frequency 3835 cm⁻¹) in POTCF (Fig.14). Same observations were made in Henningkonglwa, Kohima and Katwa samples with slight variation in frequency and number of shoulders (Figs. 15, 16 and 17 respectively).

In Jorhat samples, interesting observations were made. In CF, two strong peaks occurred at 3680 and 3600 cm⁻¹. The former peak shifted to 3690 cm⁻¹ after removing organic matter, while the latter was missing. After the samples were treated with H_2O_2 , CBD and oxalate, the strong peak at 3680 cm⁻¹ in CF disappeared. However, the 3600 cm⁻¹ peak was present in POTCF (Fig .18).

In Tamanda samples, the two peaks and one shoulder in this zone were present in CF, PTCF and POTCF with only variation in getting the peak at 3680 cm⁻¹ in POTCF as a 'strong' one, which was otherwise 'very strong' in CE and PTCF (Fig. 19).

(ii) <u>Frequencies between 3500 and 1200 cm⁻¹</u>

The peak appearing around 3400 cm⁻¹ was assigned to the - OH band. The 2920 and 2850 cm⁻¹ absorption bands were assigned to aliphatic C-H groups (Dudas and Pawluk 1969/1970). The peaks near 2300 cm⁻¹ were due to Si-H stretching frequency (Rich and Kunje 1964). Besides, the following bands were observed in the above-mentioned frequency range: 1725 cm⁻¹ (C=0 of CO₂H, C=0 stretch of ketonic C=0), 1630 cm⁻¹ (aromatic C=C / hydrogen bonded C=0 of carbonyl or quinone, COO⁻), 1450 cm⁻¹ (aliphatic C-H), 1400 cm⁻¹ (COO⁻, aliphatic C-H), 1200 cm⁻¹ (C-O stretch of OH-deformation of CO₂H) (Schnitzer 1978).



Figure 12. Infrared spectra of 2-0.05 µ fraction of an Entisol (Bentlu)



Figure 13. Infrared spectra of 2-0.05 µ fraction of an Alfisol (Naddi)



Figure 14. Infrared spectra of 2-0.05 µ fraction of an Alfisol (Palampur)



Figure 15. Infrared spectra of 2-0.05 µ fraction of an Alfisol (Henningkonglwa)



Figure 16. Infrared spectra of 2-0.05 µ fraction of an Ultisol (Kohima)



Figure 17. Infrared spectra of 2-0.05 μ fraction of an Entisol (Katwa)



Figure 18. Infrared spectra of 2-0.05 µ fraction of an Entisol (Jorhat)



Figure 19. Infrared spectra of 2-0.05 µ fraction of an Ultisol (Tamanda)

In Indore samples, the peak at 3370 cm-1 was shifted to 3400 cm-1 after peroxide treatment, while the cleaned clay registered this band at 3358 cm⁻¹ (Fig.6). The peak intensity remains unchanged. The intensity of the 1650 cm⁻¹ peak decreased after organic matter destruction with hydrogen peroxide and almost vanished in cleaned clay (POTCF). The 1434 cm⁻¹ peak vanished in PTCF and POTCE. The 1390 cm⁻¹ band (COO/ aliphatic C-H) intensity in PTCF (very small in the untreated complex) decreased after the sample was treated with CBD and NH₄-oxalate. The 1217 cm⁻¹ peak was absent in PTCF and POTCF.

In the Siraguppa sample, the 3350 cm⁻¹ band intensity remained the same in CF, PTCF and POTCE; only the band shifted to 3360 cm⁻¹ (PTCF) and 3400 cm⁻¹ (POTCF). 1650 cm⁻¹ band remained the same throughout the treatments. The 1582 cm-1 peak at CF shifted to 1600 cm-1 after organic matter destruction and to 1690 cm-1 after the removal of iron oxides and amorphous material. The 1418 cm⁻¹ band decreased from CF in PTCF and POTCF. The 1200 cm⁻¹ peak intensity decreased in PTCF, and it is missing in POTCF (Fig.7). In Nandyal (Vertisol), the OH band in the untreated complex was observed in 3415 and 3390 cm⁻¹ which remained the same after organic matter removal. The band was registered at 3380 cm⁻¹ (even stronger one) after the sample was cleaned of iron oxide and amorphous materials. The 1648 and 1620 cm⁻¹ bands remained unchanged after H₂O₂ treatment. Surprisingly, unlike in other samples, these bands were missing in cleaned clay. After organic matter destruction, the 1432 cm-1 peak shifted to 1400 cm-1 (Fig.8).

In the Mohitnagar soil samples, the very strong OH-band suffered a small change in intensity on H_2O_2 treatment, but the intensity changed significantly in POTCE. The strong band at 1601 cm⁻¹ shifted to 1617 cm⁻¹ after the H_2O_2 treatment and to 1595 cm⁻¹ after the samples were made free from iron oxides and amorphous materials. The 1433 and 1418 cm⁻¹ bands in CF shifted to 1392 cm⁻¹ with no change in intensity. In POTCF a very weak band at 1395 cm⁻¹ was registered. The 1218 cm⁻¹ shoulder peak (C-0 stretch of OH-deformation of CO₂H) was registered only in the untreated complex (Fig. 9).

The shoulder at 3450 cm⁻¹ in CF and PTCF was missing in the POTCF of the Karnal sample. The strong band due to -0H gradually shifted to a higher frequency from 3400 cm⁻¹ to 3410 and 3420 cm⁻¹ in PTCF and POTCF, respectively. 1634 cm⁻¹ (aromatic C=C/hydrogen bonded C=0 of carboxyl or quinone, COO⁻¹) band in CF shifted to 1610 cm⁻¹ after H₂O₂ treatment. After organic matter removal, the 1433 cm⁻¹ (aliphatic C-H) band shifted to a very lower frequency at 1398 cm⁻¹. The 1222 cm⁻¹ (shoulder) shifted to 1260 cm⁻¹ (shoulder) after the complex was treated with H₂O₂. Due to organic functional groups, these bands were missing in the peroxide-oxalate-treated complex (Fig. 10).

In Chikballapur red soil samples, the strong band of OH at 3410 cm⁻¹ in untreated samples became very strong at 3385 cm⁻¹ after organic matter removal. When the clay was cleaned completely, the band was registered again at a higher frequency but with much-reduced intensity at 3430 cm⁻¹. 1650 cm⁻¹ band did not change after the H₂0₂ treatment, which was missing in the peroxide-oxalate treated complex. The 1618 cm⁻¹ strong band shifted to 1600 cm⁻¹ with much-reduced intensity after organic matter destruction by H₂O₂. A very weak peak registered at 1219 cm⁻¹ disappeared when the samples were treated with peroxide and peroxide-oxalate. Like Karnal and Nandyal samples, the peroxideoxalate treated complex also failed to register bands in the 1700-1200 cm⁻¹ frequency zone (Fig.11).

The 3420 cm⁻¹ (OH band) very strong absorption band shifted to 3395 cm⁻¹ without any significant decrease in intensity after H₂O₂ treatment in Bentlu samples. Removing iron oxides and amorphous materials caused the band to change to a higher frequency at 3450 cm⁻¹ with the same intensity. There were shoulders in all three cases at 2900 cm⁻¹, which is due to aliphatic C-H groups (Dudas and Pawluk 1969/1970). The 1650 cm⁻¹ medium-intensity band weakened after removing organic matter and was absent in the cleaned complex. The strong 1618 cm⁻¹ band shifted to a lower frequency at 1598 cm⁻¹ with lower intensity after H₂O₂ treatment, which was also missing in POTCF. The 1433 cm⁻¹ (aliphatic C-H) band was absent in PTCF and POTCF (Fig.12). In Naddi samples, the strong-OH band at 3400 cm⁻¹ shifted to 3415 cm⁻¹ after organic matter destruction and removal of iron oxide and amorphous substances. However, upon organic matter removal, this peak was not observed in this case. Instead, the PTCF sample registered several shoulders at 3390, 3295, 3080 and 2950 cm⁻¹. 1650 cm⁻¹ peak (aromatic C=C/hydrogen bonded C=0 carboxyl, or quinone/COO⁻) is present in PTCF. The 1620 cm⁻¹ peak was present in both CF and PTCF. 1431 cm⁻¹ (aliphatic C-H) and 1418⁻¹ bands in CE were missing in POTCF in the peroxide-treated complex. However, the 1433 cm⁻¹ band was found. The 1216 cm^{-1} (C-O stretch of OH-deformation of CO₂H) was observed only in peroxide-treated complex (Fig.13). This is a clear indication that usual H₂O₂ treatment leaves enough organic matter with C=C and C=O functional group to be easily detected by IR. In Palampur samples, the 3450 cm⁻¹ (-OH band) strong absorption band shifted to 3420 cm⁻¹ after organic matter destruction, which moved further to 3405 cm⁻¹

¹ when the sample was cleaned from iron oxides and amorphous materials. There were shoulders at 2975 and 2925 cm⁻¹ in the untreated clay-organic complex. Shoulders at 2900 and 2905 cm⁻¹ were observed in PTCF and POTCF (aliphatic-OH groups). The 1651 intensity when the sample was made free from organic matter. This peak was missing in POTCF. 1436 cm⁻¹ (aliphatic-CH band) band was missing in the treated complex. After peroxide treatment, however, several shoulders and medium intensity bands were observed at 1398, 1389, 1379 and 1308 cm^{-1, missing in untreated complex and untreated one. A weak band at 1258 cm⁻¹ was registered in the treated complex. This was missing in the untreated complex (Fig. 14).}

In Kohima samples, the strong -OH at 3360 cm⁻¹ shifted to 3400 cm⁻¹ after peroxide treatment and to 3415 cm⁻¹ after removing organic matter, iron oxides and amorphous materials. After organic matter destruction, several shoulders are at 3300, 3240 and 3210 cm-1. A shoulder at 2900 cm⁻¹ (aliphatic C-H group) was registered in POTCF, which was otherwise missing in the untreated and peroxide-treated complex. After peroxide treatment, 1654 and 1596 cm-1 bands (aromatic C=C, hydrogen bonded C-O of carboxyl or quinone, COO-) shifted to 1650 cm-1 and 1616 cm-1. Two weak bands at 1438 and 1423 cm⁻¹ in the untreated complex were absent in the treated one. One medium intensity band at 1398 (COO⁻ , aliphatic C-H) cm⁻¹ was observed in PTCF. The shoulder peak at 1220 cm⁻¹ in CF (C-O stretch of OHdeformation of CO₂H) was absent in the peroxide-treated complex (Fig.16).

The strong -OH band at 3405 cm⁻¹ was slightly shifted to 3400 cm⁻¹ after organic matter removal in Jorhat samples, which again was shifted to 3420 cm⁻¹ after the removal of organic matter, iron oxides and amorphous materials. Several shoulders in untreated complex at 3235, 3150, 2900 and 2800 cm⁻¹ were not found in the treated complex. 1650 and 1620 cm⁻¹ bands suffer a decrease in intensity and shift to 1650 and 1612 cm⁻¹ in PTCF. Two bands at 1431 and 1428 cm⁻¹ were observed in CF. However, these bands were missing in peroxide-treated clay, which registered a weak band at 1395 cm⁻¹ (COO⁻, aliphatic C-H) (Fig. 18).

The 3390 cm⁻¹ band was shifted to 3400 cm⁻¹ in a treated complex in the case of Katwa samples. The medium intensity peaks at 1652, 1630, and 1620 cm⁻¹ shifted to 1650, 1635 and 1609 cm⁻¹ when organic matter was removed from the complex. The cleaned clay did not register any band in this zone. The 1432 cm⁻¹ band (aliphatic C-H) was shifted to 1418 cm⁻¹ in PTCF, thus showing a slight decrease in intensity. The shoulder band at 1214 cm⁻¹ in the untreated clay-organic complex was absent in the peroxide-treated complex and in cleaned clay (Fig.17).

In the Henningkonglwa sample, the -OH band appeared at 3350 cm⁻¹ and was shifted to 3400 cm⁻¹ when subsequent treatments were followed. There were two shoulders at 2985 and 2700 cm⁻¹ in CF and 3250 and 3095 cm⁻¹ in POTCF. The 1650 and 1587 cm⁻¹ bands were shifted to 1651 and 1614 after organic matter destruction and were absent in the cleaned complex. Due to aliphatic-CH or COO, the 1431 and 1419 cm⁻¹ bands appeared at 1398 cm⁻¹ with weak intensity in PTCF. The 1213 cm⁻¹ shoulder band in the untreated complex could not be observed in the treated complex (Fig.15).

In the case of the Tamanda sample, a strong -OH band at 3415 cm⁻¹ in CF occurred at 3410 cm⁻¹ and 3420 cm⁻¹ in PTCF and POTCF, respectively. The 2900 cm⁻¹ shoulder band (aliphatic C-H group) was present in all three cases. 1648 and 1620 cm⁻¹ bands were only slightly shifted to 1650 and 1621 cm⁻¹ in PTCF with a reduction in 1650 cm⁻¹ band intensity. These bands were absent in the cleaned complex. After organic matter removal, the 1400 cm-1 weak band was shifted to 1398 cm-1 (COO-, aliphatic-CH). A very weak absorption band at 1260 cm⁻¹ observed in peroxide-treated complex was absent in the other two cases (Fig.19).

The disappearance of the shoulders in Indore, Kohima and Nandyal samples may be due to (1) the restored symmetry of the crystalline counterpart as the surface of the minerals was gradually cleaned and/or (2) the decrease in the content of functional groups (-OH) which are also present in organic matter, free oxides and amorphous materials. The 3650 cm⁻¹ band appeared in all cases, even with different treatments. The gradual decrease in intensity of 3680 and 3600 cm⁻¹ bands (Tamanda, Chikballapur) may be due to removing the –OH groups from the complex because the treatments successively removed organic matter, free oxides and amorphous materials. The strong and sharp bands at 3680 cm⁻¹ observed in the (Chikballapur, Tamanda and Jorhat) untreated sample, which showed an increase in the intensity with different treatments, may be caused by uncovering the edge-OH groups of kaolinites in these kaolinite dominant soils.

The structural –OH band around 3400 cm⁻¹ in Indore, Palampur, and Katwa samples has shifted to lower frequencies stepwise as the treatments were given. In Bentlu, Naddi, Jorhat and Tamanda samples, this band shifted towards low frequency on peroxide treatment, which again became higher when peroxide-CBD-oxalate treatments were given. Mohitnagar sample registered no change, while the rest gave variable shifts with no definite order. So far, the intensity of this band was concerned; it first increased in PTCF and then again decreased in Indore, Karnal, Palampur, Nandyal, Henningkonglwa and Kohima samples. In Chikballapur, Bentlu and Naddi samples, the intensity decreased with the treatments. The intensity did not change in PTCF but decreased when CBD-oxalate treatments were given in Mohitnagar, Jorhat, Katwa and Tamanda samples. In Siraquppa, no such change was observed.

The increase in the intensity of this band may be due to the rise in the relative proportion of the amorphous oxides in the clay-organic complex on peroxide treatment; the removal of the latter again decreased the intensity. Such was the case with Indore, Karnal, Palampur, Nandyal, Kohima and Henningkonglwa samples. The stepwise decrease in the intensity suggests removing the functional groups with the treatments. This might also be due to the removal of the complex-forming functional groups. In a few samples, no change in band intensity in the peroxide-treated samples may be due to the removal of only the free organic matter, which was not associated with the mineral counterpart.

However, the subsequent treatment decreased its intensity. This may be due to the removal of the amorphous oxides and the organic matter associated with these oxides. Such a condition was observed in Mohitnagar, Jorhat, Katwa and Tamanda samples.

Except in Tamanda and Kohima samples, the 1640 cm⁻¹ was found in the clay-organic complex and peroxide-treated samples. In Karnal and Palampur, this band appeared as a shoulder due to organic matter removal. By and large, removing organic matter in all the samples decreased the 1600 cm⁻¹ band intensity. Karnal, Indore and Siraguppa were exceptions, where the reverse occurred. The band at 1600 cm⁻¹ was largely due to carboxylate ions, which persisted in a dark clay-organic fraction resistant to alkaline extraction (Kumada and Aizawa 1959). After oxidation of the organic matter with hydrogenperoxide, the spectra of the clays showed the presence of adsorbed oxalate ions, the amount of which increased as the proportion of amorphous oxides in the clay increased (Farmer and Mitchell 1963). These observations suggest that much of the organic matter is held by ionic bonding between carboxylate ions and iron or aluminium ions on the surface of amorphous oxides, which may be discrete entities or surface coatings on layer silicates. Clean layer silicates have little tendency to bond carboxylate ions (Yariv et al. 1966). However, the expanding layer silicates can hold neutral or basic organic molecules in their interlayer space, but there is no evidence that this occurs under natural conditions.

The complete disappearance of the 1430 cm⁻¹ PTCF in Mohitnagar, Henningkonglwa and Indore samples might suggest that H_2O_2 was more successful in removing the organic matter. In other words, these samples' organic matters are relatively more easily oxidizable. In Karnal, Katwa, Bentlu, Jorhat, Kohima, Palampur and Nandyal samples, this band, on peroxide treatment, appeared either as shoulder or with decreased intensity with a slight shift. The relatively greater decrease in surface area values on peroxide treatment in Henningkonglwa, Palampur, Bentlu, Mohitnagar, and Karnal samples find support from these infrared observations.

(iii) Frequencies between 1150 and 400 cm⁻¹

In Indore soil samples, the 1013 cm⁻¹ band shifted to 1020 cm⁻¹ after organic matter destruction and again to 1010 cm⁻¹ after removing organic matter, iron oxides and amorphous constituents. Besides, one shoulder at 1152 cm⁻¹ opened up after organic matter removal, which was otherwise observed in CF and POTCF (Fig.6).

The absorption bands observed in this region have been described by Farmer and Russell (1964) as due to lattice vibration. In this range, the layer silicates in which aluminium-for-silicon substitution is absent or low give the sharpest spectra. The figure after Stubican (1963), shows this investigator's assignment of bands in this region. Minerals with low aluminium-for-silicon substitution show a similar

absorption pattern in the 1150-960 cm⁻¹ region, arising from Si-O stretching vibrations. A comparison of the spectra of oriented and random samples shows three well-defined medium or strong in-plane vibrations and one perpendicular vibration for each sample.

In the Indore sample, the shoulder band was at 900 cm-1 in CF, and the POTCF shifted to 906 cm-1 in PTCF. 927 cm⁻¹ shoulder was present only in PTCF. 862 cm⁻¹ shoulder only changed to 868 cm⁻¹ and 864 cm⁻¹ in PTCF and POTCE respectively. Weak bands were detected in 788, 749, 686 and 607 cm⁻¹ in untreated samples, while in peroxide-treated samples, these were at 790, 762, 749 (very, very weak) and 690 (shoulder) cm⁻¹. After peroxide treatment, the 510 and 500 cm-1 bands were shifted to 520 and 510 cm-1. The cleaned complex detected only a shoulder at 516 cm⁻¹ (Fig.6).

Vibrations in the 960- to 550 cm⁻¹ region are attributed to R-0-H bending vibrations. Comparison of the spectra of normal kaolinite and nontronite with synthetic minerals containing deuterium in place of hydrogen has established that the bands near 935 and 914 cm⁻¹ in the kaolinite minerals and those at 848 and 819 cm⁻¹ in nontronite arise from OH bending vibrations (Stubican and Roy 1961). By analogy the same assignment can be given to the absorption bands at 950 cm⁻¹ in Pyrophyllite, 942 cm⁻¹ in beidellite, and 915 to 920 cm⁻¹ in montmorillonite. Smectites with high iron content show an absorption band at 870 cm⁻¹, and there appears to be a correlation between the intensity of this band and iron content. Possibly, the 848 cm⁻¹ band in nontronites, like the 870 cm⁻¹ band in montmorillonites, arises from hydroxyl groups shared between ferric iron and aluminium in the octahedral layer. A bending frequency of hydroxyl groups shared between aluminium and magnesium might be expected in the spectra of montmorillonite, and the band at 850 cm⁻¹ may have this assignment. However, this is by no means certain. The strong absorption in the region below 550 cm⁻¹ must arise principally from in-plane vibrations of the octahedral ions and their adjacent oxygen layers. These vibration couples give modes which can equally well be described as metal-oxygen stretching or siliconoxygen bending. Farmer and Russell (1964) stated that substituting aluminium for silicon in the tetrahedral layers does not greatly shift the main absorption bands in this region, and it must be concluded that the octahedral cation's nature and distribution largely determines the absorption pattern. The presence of iron and magnesium replacing aluminium causes a shift of these absorption bands to lower frequency and/or the development of a new absorption band, as in the case of nontronite at 430 cm⁻¹. Besides, montmorillonite bands at 568, 523, 521, 473, 468 and 430 cm⁻¹ were reported by Farmer and Russell (1964).

In the octahedral sites of dioctahedral minerals with increasing amounts of magnesium, the H-O-Al absorption band at 935 cm⁻¹ decreases in intensity and is more poorly resolved, and the frequency and intensity of the Si-O-Al VI band at 535 cm⁻¹ decrease. With trioctahedral clay minerals, the bands mentioned above are absent. A very strong peak at 451 cm⁻¹ in CF was shifted to 458 cm⁻¹ with no change in band intensity, while POTCF registered it at 458 cm⁻¹ with a much lower intensity. There were shoulders at 462 and 416 cm⁻¹ in CF and 465 and 414 cm⁻¹ in PTCF of Indore samples (Fig.6).

In the Siraquppa the 1008 cm⁻¹, strong absorption band shifted to 1106 cm⁻¹ after organic matter destruction and came back to 1015 cm⁻¹ when the samples were almost cleaned of organic matter, iron oxides and amorphous materials (Fig.7).

One shoulder appeared at 1100 cm⁻¹ in the untreated sample only in the case of Siraguppa soil. There were two shoulders in CF at 897 and 853 cm^{-1,} while in POTCF, there were bands at 924, 908, 890, and 864 cm⁻¹. In PTCF no such shoulders were observed. The 687 cm⁻¹ medium intensity band was shifted to 690 cm⁻¹ and 683 cm⁻¹ at PTCF and POTCE, respectively, with much reduced intensity. The 458 cm⁻¹ strong band was shifted to 460 cm⁻¹ after peroxide treatment. Cleaned clay registered this band at 458 cm⁻¹ again. One weak band at 510 cm⁻¹ appeared, which was absent in two other cases. There were three shoulders in CF at 546, 514, 506 and 508 cm⁻¹ in PTCF and 552 and 525 cm⁻¹ in POTCF. 421 cm⁻¹ shoulder came in CF and PTCF.

In Nandyal samples, the 1010 cm⁻¹ strong absorption band shifted to 1018 cm⁻¹ after organic matter destruction (Fig.8). Cleaned sample registered it at 1012 cm⁻¹. Shoulders were registered at 932, 922, 909, 870 cm-1 in CF, 990, 908, 875, 829 cm-1 in PTCF and 970, 904 and 871 cm-1 in POTCF. 790, 773, 691 and 664 cm⁻¹ weak bands were shifted to 791, 773, and 691 cm⁻¹ in PTCF. Cleaned clay failed to register these bands. The strong band at 458 cm⁻¹ shifted to 465 cm⁻¹ in PTCF and returned to 458 cm⁻¹ in POTCF. The 518 cm⁻¹ band in untreated clay became strong at 515 cm⁻¹ after the destruction of organic matter with increased band intensity. Cleaned clay had the same peak at the same frequency. In the uncleaned sample, the bands 523 (sh), 518, 507, 468 (sh), 448 (sh) and 420 (sh) cm⁻¹ were observed.

In the Mohitnagar sample, two strong bands nearby appeared at 1007 and 995 cm⁻¹ in untreated condition (Fig. 9). Peroxide treated sample registered it at 1006 cm⁻¹. There appeared shoulders in CF at 1130 and 1074 cm⁻¹, in PTCF at 1114 cm⁻¹, POTCF at 1061 cm⁻¹. Below 1000 cm⁻¹ zone (R-OH bending frequency) absorption bands at 930 (sh), 793, 778, 658, 649, 589 (sh), 578 (sh) and 558 (sh) cm⁻¹ were recorded in CF; 911 (sh), 792, 776, 744, 692, 668, 618 (sh), 592 (sh), 578 (sh) and 550 (sh) cm⁻¹ were recorded in PTCE; 966 (sh), 902 (sh) and 836 (sh) cm⁻¹ in POTCF were observed. Two strong bands were observed in CF at 477 cm⁻¹ and 467 cm⁻¹, one at 466 cm⁻¹ in PTCF and one at 458 cm⁻¹ in POTCF. One medium-intensity band, however, appeared in the cleaned sample at 472 cm⁻¹. There were weak bands at 522 cm⁻¹ in CF, 526, 579, 508 cm-1 in PTCF, and 515 cm⁻¹ in POTCF. The shoulder at 432 cm⁻¹ in the untreated sample shifted to 423 cm⁻¹ in the peroxide-treated sample.

The strong band at 1000 cm⁻¹ shifted to 1010 cm⁻¹ in peroxide-treated sample and to 998 cm⁻¹ in cleaned sample in case of Karnal soils, shoulders appeared at 1158 and 1054 cm⁻¹ in CF, 1153 and 1064 cm⁻¹ in PTCE and at 1158 cm⁻¹ in POTCF (Fig. 10). Below 1000 cm⁻¹ frequency region (R-OH bending frequency) bands at 910 (sh), 821, 793, 773, 747, 721, 692 and 669 cm⁻¹ in CF; at 982 (sh), 940 (sh), 905 (sh), 793, 774. 746, 692 and 669 cm⁻¹ in PTCF; at 974 (sh), 906 (sh) and 870 (sh) cm⁻¹ in POTCF were observed. The strong band at 464 cm⁻¹ was slightly shifted to 466 cm⁻¹ in treated samples. One medium intensity band at 521 cm⁻¹ shifted to 520 cm⁻¹ in PTCF and 512 cm⁻¹ in POTCF. Shoulders at 428 cm⁻¹ in CF and 413 cm⁻¹ in PTCF were also registered.

Quite interesting observations were made in Bangalore's Chikballapur red soils (kaolinitic). The 1098 cm⁻¹ medium intensity bands (Si-O stretching for kaolinite) (Rich and Kunje 1964) became very stong when organic matter was removed. The band intensity remained the same but shifted to 1080 cm⁻¹ cleaned sample (Fig.11). Two distinct bands at 1023 and 1000 cm⁻¹ (equally strong) became more pronounced when the samples were cleaned with a slight shift towards lower frequency in POTCF. The sharpness and resolution of these bands conformed with the dominance of kaolinite in the clay sample. It also indicated the dominance of relatively smaller particles in the sample. The 904 cm⁻¹ (-OH bending vibration) band shifted to 903 cm⁻¹ (PTCF) and to 900 cm⁻¹ (POTCF). The 688 cm⁻¹ strong band in the untreated sample shifted to 684 cm⁻¹ band shifted to 528 cm⁻¹ in the peroxide-treated sample, and when the sample was cleaned, the band appeared at 522 cm⁻¹ with still higher intensity. The observation with the band at 460 cm⁻¹ ultimately shifted to 457 cm⁻¹ in POTCF. A medium intensity band at 426 cm⁻¹ in CF and PTCF shifted to 414 cm⁻¹ in POTCF.

The position and sharpness of the perpendicular vibration vary with physical state; thus in the spectra of kaolinite of large crystal size, this mode appears as a broad shoulder near 1080 cm⁻¹. The band intensifies and shifts to higher frequencies in the spectra of smaller crystals until the band is at 1109 cm⁻¹ in very finely ground material.

In pyrophyllite, the frequency of the perpendicular node is 1052 cm-1, which is considerably lower than that found in kaolinite minerals (about 1109 cm⁻¹). The two strongest in-plane vibrations occur in the 1037 to 1018 cm-1 frequency range and are about the same in the kaolinite and montmorillonite minerals. Still, for pyrophyllite, it lies at a much higher frequency (mean 1061 cm⁻¹), suggesting a significantly different structure. The third high-frequency in-plane vibration in the 1150-960 cm⁻¹ region occurs within a relatively narrow range from 1121 to 1100 cm⁻¹ in most minerals examined.

In Bentlu samples, 1014 cm⁻¹ strong band shifted to 1006 cm⁻¹ after organic matter removal and to 1015 cm⁻¹ in the cleaned sample (Fig.12). Number of shoulders appeared in cleaned samples at 1157,

1110, 1104, 1095, and 1075 cm⁻¹. In CF and PTCF, 1093 and 1090 cm⁻¹ shoulder bands were registered. Below 1000 cm⁻¹ frequency in CF bands were observed at 937 (sh), 905, 820, 790, 773, 747 and 689 cm⁻¹, in PTCF 940 (sh), 903, 790, 776, 747, 688, 618 (sh), 590 (sh), 573 (sh) cm⁻¹, in POTCF 901, 898, 877, 690 and 620 cm⁻¹. The 529 cm⁻¹ strong band shifted to 470 and 460 cm⁻¹ in PTCF and 468 cm⁻¹ in POTCF. Besides, one weak band at 428 cm⁻¹ in untreated samples was observed, which was absent in treated samples except in PTCF, where a shoulder at 423 cm⁻¹ was observed.

In Naddi samples, the 1010 cm⁻¹ strong band in CF decreased in intensity in PTCF and shifted to 1003 cm⁻¹, but on removal of free oxides and allophane the intensity increased appreciably (cf. POTCF) and shifted to 1010 cm⁻¹ (Fig. 13). The 904 cm⁻¹ band increased in intensity as it was made free from organic matter, iron oxides and amorphous materials but only organic matter removal did not bring about much change in band intensity. Shoulder bands at 1153, 1082 and 1070 cm⁻¹ in CF, 1157 and 1070 cm⁻¹ in PTCF, and 1073 and 1041 cm⁻¹ in POTCF were observed. 821 cm⁻¹ band shifted to 820 cm⁻¹ in POTCF. It was absent in peroxide-treated samples. The 790 cm⁻¹ absorption band shifted to 790 cm⁻¹ in the peroxide-treated sample and to 792 cm⁻¹ in the cleaned sample with still higher intensity. When the samples were cleaned, the 688 cm-1 band shifted to 690 cm-1 in PTCF and gave rise to 690, 678 and 664 cm-1 bands. In untreated samples, the 523 cm⁻¹ absorption band gave rise to three bands at 522, 518 and 508 cm⁻¹ in PTCF, and it increased in intensity when the samples were cleaned and appeared at 522 cm⁻¹. Similar was the case with the 463 cm⁻¹ absorption band. The shoulder band was at 420 cm-1 and 422 cm-1 in CF, and the PTCF shifted to 413 cm⁻¹ with a well-pronounced absorption band.

In the case of Palampur samples, strong bands at 1033 and 1014 cm⁻¹ in untreated sample shifted to 1014 cm⁻¹ in peroxide-treated sample and to 1010 cm⁻¹ in peroxide-oxalate treated complex (Fig.14). The shoulder bands appeared at 1160, 1070 cm⁻¹ CF; 1156, 1143 and 1061 cm⁻¹ in PTCF; 1153 and 1071 cm⁻¹ in POTCF. Below 1000 cm⁻¹ frequency the bands at 911 (sh), 826, 797, 778, 750, 711 (sh), 693, 670, 620 (sh), 610 (sh) cm⁻¹ in CF; 907 (sh), 853 (sh), 820, 794, 773, 748 and 690 cm⁻¹ in PTCF, 904 (sh), 820, 790, 772, 740, 662 and 638 cm⁻¹ in POTCF were observed. 530 cm⁻¹ strong band shifted to 526 cm⁻¹ after organic matter destruction and to 521 cm⁻¹ after organic matter, iron oxide and amorphous material removal. With increasing intensity, the 471 cm-1 band shifted to 460 cm-1 in PTCF and to 463 cm-1 in POTCF. The 431 cm⁻¹ band in POTCF was missing in CF and PTCF.

The 1011 cm⁻¹ band shifted to 1010 cm⁻¹ after organic matter destruction and to 1020 cm⁻¹ in cleaned sample from Kohima (Fig.16). Shoulder bands at 1070 cm⁻¹ in CF, 1157, 1084, 1074, 1039 cm⁻¹ in PTCF; 1158, 1077, 1055 cm⁻¹ in POTCF. The 792 cm⁻¹ peak in CF shifted to 790 cm⁻¹ in PTCF and to 792 cm⁻¹ in POTCF- band intensity increasing with each treatment. The weak bands here in this zone were 774, 749, 690, 670 (sh), 621 (sh) cm⁻¹ in the untreated sample; 770, 740, 689, 624 (sh), 618 (sh)

cm⁻¹ in the peroxide-treated sample; 739, 688, 640 (sh) and 553 (sh) cm⁻¹ in POTCF. The increasing sharpness and peak intensity were observed as the sample treatment started at 522 cm⁻¹, 478 cm⁻¹ in CF, 530 cm⁻¹, 475 cm⁻¹ in PTCF and 527 cm⁻¹ and 469 cm⁻¹ in POTCF. No clear bands were observed below 500 cm⁻¹ frequency.

In Jorhat samples, two distinct bands at 1023 and 1000 cm⁻¹ in CF became pronounced at 1020 cm⁻¹ and 1000 cm⁻¹ (like Chikballapur red soils) when samples were cleaned completely (Fig. 18) . Several shoulders at 1158, 1121, 1102, 1097, 1087, 1072 cm⁻¹ in CF; 1096 and 1080 cm⁻¹ in PTCF; 1157 and 1060 cm⁻¹ in POTCF were registered. 908 cm⁻¹ band weakened at 904 cm⁻¹ after organic matter removal and subsequent sample cleaning. The 988 cm⁻¹ shoulder band shifted to 990 cm⁻¹ in PTCF and was missing in POTCF. Below 1000 cm⁻¹ frequency other bands were 840, 834, 825, 794, 786, 774, 755, 748, 743, 720, 690, 633, 591, 580 and 573 cm⁻¹ in CF; 792, 772, 750 and 690 cm⁻¹ in PTCF; 904, 791, 774, 747, 666 and 630 cm⁻¹ in PTCF. The sharpness and intensity had been increased in bands at 531, 466 cm⁻¹ in CF; 528 and 467 cm⁻¹ in PTCF; 525 and 464 cm⁻¹ in PTCF; 525 and 464 cm⁻¹ in PTCF.

In the case of the Katwa sample, the peak around 1000 cm-1 in the untreated sample, broadened after organic matter destruction and became somewhat sharp when the sample was made clean. Shoulder bands at 1154, 1078 and 1060 cm⁻¹ were observed in the cleaned sample (Fig.17). The 688 cm⁻¹ band in CF lost its intensity when the sample was cleaned, and it suffered a shift to 690 cm⁻¹ in PTCF and to 687 in POTCF. The other bands in this zone were more or less similar, with slight shifting in frequency. Organic matter removal made the band below 550 cm⁻¹ more complex. However, these bands became sharper and clearer when the organic matter, iron oxides and amorphous materials were removed from the sample. This was especially true for the band at 460 cm⁻¹ and 467 cm⁻¹ in POTCF.

The broad absorption band centering around 1003 cm⁻¹ in CF of Henningkonglwa soil samples shifted to 1014 cm⁻¹ after organic matter destruction and finally converged to 1000 cm⁻¹ in a completely cleaned sample (Fig.15). The shoulder bands were at 1072 cm⁻¹ in CF; 1160, 1091, 1051 cm⁻¹ in PTCF and 1151 and 1040 cm⁻¹ in POTCF. Below 1000 cm⁻¹ frequency the bands were at 969 (sh), 935 (sh), 900(sh), 815, 790, 770, 743, 685, 664 and 629 cm⁻¹ in untreated sample; at 974 (sh), 793, 776, 690 and 621 (sh) cm⁻¹ in peroxide-treated sample; at 905 (sh), 820 (sh), 790, 771, 740, 663 and 630 cm⁻¹ in peroxide-oxalate treated sample. The 470 and 460 cm⁻¹ bands merged at 474 in POTCF with a shoulder at 453 cm⁻¹. Similarly, 524, 518, and 506 cm⁻¹ bands gave rise to a single band at 527 in PTCF and 523 and 518 cm⁻¹ in POTCF.

In case of Tamanda sample, two adjacent bands at 1030 and 1002 cm⁻¹ in CF shifted to 1025 and 1003 cm⁻¹ in PTCF and became more distinct and resolved at 1026 and 1003 cm⁻¹ in POTCF (Fig.19). The shoulder bands (Si-O stretching) were 156, 1100, 1061 cm⁻¹ in CF; 1155, 1096 and 1052

cm⁻¹ in PTCF; 1158, 1100, 1058 cm⁻¹ in POTCF. The 908 cm⁻¹ absorption band decreased in intensity with each treatment given. The same was true to the band at 793 (CE), 792 (PTCF) and 791 (POTCF) cm⁻¹. Other bands were similar. The 690 cm⁻¹ band lost its sharpness as the samples were treated with peroxide and peroxide-CBD-oxalate. The 532 and 468 cm⁻¹ bands were relatively broad in CF and gradually became sharp as the treatments continued. These were 531 and 467 in PTCF and 530 and 465 cm⁻¹ in POTCF. 428 cm⁻¹ band shifted to 424 cm⁻¹ in POTCF and was missing in the peroxide-treated sample.

The removal of organic matter and amorphous oxides shifted the 1000

cm⁻¹ band to higher frequency in Nandyal, Siraguppa, Kohima and Henningkonglwa samples. This shifting was perhaps due to the coupling of the frequency of silicate minerals and amorphous materials which would now absorb at a relatively higher frequency. The Si-O band for allophone and silicic acid would appear at a relatively higher frequency. As a result of the removal of organic matter, the vibration of Si-O groups in allophane and silicic materials and silicate crystals would increase.

The band around 1000 cm⁻¹ shifted to a higher frequency. When organic matter was removed, the shift was maximum (14 cm-1) in Henningkonglwa. This was also appreciable in the Nandyal (8 cm⁻¹) sample. Removal of organic matter, however, resulted in a very little shift in Siraguppa and Kohima samples. This suggests that the functional groups of organic matter are more associated with mineral surfaces in Henningkonglwa and Nandyal samples. The CBD-oxalate treatment resulted in higher shifts in the Siraquppa (7 cm⁻¹) and Kohima (10 cm⁻¹) samples. This treatment could only slightly change in Henningkonglwa and Nandyal samples. This might suggest a greater association of oxides and amorphous materials with mineral surfaces in Siraguppa and Kohima.

Except in those four samples, the other samples suffered, in general, a shift of this band towards lower frequency. On peroxide treatment, the shift was appreciable in Indore, Jorhat, Bentlu, Naddi and Palampur samples; Tamanda, Mohitnagar, Chikballapur suffered a moderate shift, while Karnal and Katwa registered no change. When CBD-oxalate treatment was given, maximum shift (20 cm⁻¹) was observed in the Jorhat sample, followed by Chikballapur (10 cm⁻¹), Naddi (7 cm⁻¹), and Mohitnagar (7 cm⁻¹). In the other samples, the shift was still less. The bands (including shoulders) in the region of 960-550 cm⁻¹ became sharp and well pronounced when organic matter was removed in Indore, Karnal, Chikballapur, Palampur, Nandyal and Kohima samples. This suggests that the organic matter is involved through its functional groups in complex formation, thereby reducing the resolution and intensity of the absorption bands in this region. Removal of organic matter helped clean the surface of the minerals, which retains much of the inorganic materials in the form of amorphous oxides. That the different treatments could not make the surface completely clean was observed when the infrared spectra of POTCF were examined. Even after CBD-oxalate therapies, all the samples retained some organic

materials, which must have been strongly complexed with the inorganic constituents, and the conventional peroxide treatment could not remove these materials. The electron microscopic studies clearly indicate the involvement of amorphous inorganic constituents with organic matter in complex formation. Unlike the samples mentioned above, Bentlu, Naddi, Jorhat, Katwa, Henningkonglwa, and Tamanda samples registered relatively weak bands in this region in the peroxide-treated samples. Peroxide possibly has oxidized organic matter more effectively in these samples.

4.4.9. <u>Studies of morphological features by Transmission Electron</u> <u>Microscope (T.E.M.)</u>

(a) Coarser fractions (2-0.05 µ) of clay-organic complex with different treatments

Some aggregates are shown in Plates 1a, 1e, 2e, 2f, 3c and 4a for Bentlu, Mohitnagar, Karnal, Katwa and Jorhat samples (all Entisols). Fig.1a depicts an aggregate of irregular elongate shape consisting of extremely small particles of minerals cemented by humus and inorganic amorphous materials in the Bentlu sample. Sonification during sample preparation has resulted in the breakdown of part of the aggregate, releasing the components. A part of the individual crystalline component can be seen at the upper left-hand corner of Plate 1a, which consists of extremely small mica particles. The aggregation of these particles through the cementing action of humus and amorphous materials can be seen more clearly at the upper edge where the aggregate is showing rupture. There are cementing materials between crystalline particles, which form a coating on the particles. In Mohitnagar, the naturally-occurring aggregates appear as highly electron-dense, relatively loosely held, irregularly shaped porous mass (Plate 1e). This was the characteristic feature of this sample.

One of the electron micrographs shows aggregation with humus particles, crystalline components, and iron oxides (Plate 2f). In Plate 2f, the formation of circular to globular aggregates by bonding of micaceous particles with organic matter and amorphous material is very clearly seen. In forming such aggregates, the development of micropores in fairly large numbers is also quite apparent. Organic matter and amorphous materials, particularly globular allophanic materials, are found to form chain-type open aggregates (Plate 2e). Heavily coated aggregates with gel-like amorphous materials were common in the Katwa sample (Plate 3c). The shape of aggregates varied and was mainly irregular. Globular and triangular-shaped aggregates forming mainly with extremely small particles, whereas the relatively larger particles aggregated into irregular forms. A typical globular aggregate with its boundary disintegrating is depicted in Plate 4a. The electron-dense nature of the central core is an indication of its globular nature. The figure also clearly indicates the involvement of a higher proportion of amorphous constituents in such aggregate.

After peroxide treatment, the particle association in the Bentlu sample could be seen more clearly. In some cases, it was with bigger and smaller particles of mica and kaolinite, with amorphous being the bridging material (Plate 1b). At the same time, iron oxide acts as a cementing material to bridge the big mica particles and as a surface coating (Plate 1c). Peroxide treatment was more effective in the Bentlu sample than in the Mohitnagar sample. In the Mohitnagar sample, which contained a very high amount of organic matter, unlike other samples, the aggregates' morphology and constituents could not be clearly assessed. Even after peroxide treatment organic matter was retained but aggregate morphology became relatively clear. The association of amorphous material with the residual organic matter in forming aggregates is conspicuous in the sample (Plate 1f). Such aggregates appeared to be highly porous. Aggregates involving crystalline particles, both small and large, in general, are globular to irregular in shape (Plate 2a). In these aggregates, organic matter also seems to have been somewhat retained, even after peroxide treatment.



PLATE 1: Electron micrographs for Bentlu and Mohitnagar samples (2-0.05 μ) BENTLU (2-0.05 μ)

(a) Aggregate coated with humus and amorphous materials * 20350 (No treatment); (b) Association of bigger and smaller particles of mica and kaolinite with amorphous materials * 12700 (Peroxide treated); (c) Association of mica particles coated with iron oxides *16280 (Peroxide treated); (d) Aggregate of different particles * 20350 (Peroxide-CBD-oxalate treated)

MOHITNAGAR (2-0.05 μ)

(e) Organic matter and iron coated aggregate *34200 (No treatment); (f) Aggregate with amorphous oxide and residual organic matter * 20350 (Peroxide treated)



PLATE 2: Electron micrographs for Mohitnagar and Karnal samples (2-0.05 μ) MOHITNAGAR (2-0.5 μ

(a) Globular to irregular shaped aggregate * 34200 (Peroxide treated) ; (b) General views of Mohitnagar clay * 46200 (Peroxide-CBD-oxalate treated) ; (c) Edge to edge bonding of coated kaolinite and mica particle * 34200 (Peroxide-CBD-oxalate treated); (d) Thin flakes of mica particles with clean surface * 34200 (Peroxide-CBD-oxalate treated); oxalate treated)

(b)

KARNAL (2-0.5 μ

(e) Globular allophanic materials forming chain type aggregate * 46200 (No treatment); (f) Circular to globular aggregates of micaceous particles with organic matter and amorphous material * 16280 (No treatment)

In the Karnal sample on peroxide treatment, the components of aggregates were more clearly visible (Plate 3a). An interesting feature was the segregation of allophonic materials into separate aggregates and that of micaceous material into bigger or smaller aggregates. The allophanic material appeared as a thin irregular mass joining to form pores. These allophanes also have iron oxides inclusions as was apparent from electron-dense areas (Plate 3a). Aggregates formed by the association of mica particles were also found in abundance in the Katwa sample. Plates 3d and 3e show the different types of mica association with amorphous materials and iron oxides. Aggregates in Plate 3d represent a situation where extremely small mica particles and large amounts of amorphous materials are involved in forming aggregate.

In Plate 3e, it can be clearly seen that smaller and bigger mica particles coated with ironoxides and allophanes form oval-shaped aggregates. Aggregates consisting of globular allophane particles are the distinctive feature observed in the Jorhat sample on peroxidation (Plate 4c). From the samples, more clear evidence of preponderance of globular aggregates of smaller and bigger sizes was observed; many aggregates with a heavy coating of iron oxides were also detectable. In Plate 4b, such a situation is depicted. Circular, angular and irregularly shaped aggregates are presented, comprising different particles not easily identifiable except the mica particles near the centre. The diameter of the aggregates are in the range of $1-2 \mu$.

After CBD-oxalate treatments, the surfaces of relatively large-sized mica particles became clean, and their morphology was visible. However, particles smaller than 0.5 µ still seemed to have retained some coating of amorphous materials and iron oxides and still tend to form aggregated mass (Plate 1d). In contrast, the bigger-sized particles could be seen as individual particles, particularly the mica particles. In the Mohitnagar sample, the oxalate treatment also brought about the particles' detailed morphology very clearly. In Fig. 2b, the clean surface of a well-crystalline hexagonal kaolinite particle can be seen. Thin flakes of mica with its fracture and cleaned surface were also clearly visible (Plate 2d). In contrast, in some instances, mica and kaolinite particles retain the coatings of iron and amorphous oxides and tend to keep their aggregated structure. The edge-to-edge bonding of a coated kaolinite particle with a coated mica particle is shown in plate 2c. This figure also shows a highly electron-dense aggregate, indicating the failure of the oxalate treatment in removing the iron oxides from some aggregates. This also shows that iron oxide involved in aggregate formation does not have the same solubility in this reagent. This aspect of differential solubility of iron oxides in different aggregates needs further investigation. Though the effect of oxalate treatment was more or less similar in the Karnal sample, it was also found that many of the clay mineral particles, residues of oxides, and allophones persisted on the surface. Such evidence is shown in Plate 3b. Oxalate-treated sample



PLATE 3: Electron micrographs for Karnal and Katwa samples (2-0.05 μ) KARNAL (2-0.5 μ

(a) Mica coated with oxides *27470 (Peroxide treated); (b) Cleaned mica particles *34200 (Peroxide-CBD-oxalate

treated)

KATWA (2-0.05 μ)

(c) Heavily coated aggregates with amorphous materials *46200 (No treatment) : (d) Aggregates of mica and amorphous materials* 16280 (Peroxide treated); (e) Oval shaped aggregate with iron oxides and allophane *16280 (Peroxide treated);
(f) An aggregated mass *34200 (Peroxide-CBD-oxalate treated)

in Katwa revealed the morphology of well-dispersed particles. The mica surface is relatively cleaner than the kaolinite particles, which are smaller than mica. Smectites appear as highly dispersed materials, looking more like amorphous substances. In Plate 3f, an aggregated mass of mica particles is presented on which extremely small particles of kaoline with rounded edges are also superimposed. At the upper left-hand corner of the figure, a discrete kaolinite particle and an aggregated mass of finer particles involving smectites can be seen. In the Jorhat sample, the oxalate treatment, while bringing out the morphology of clay particles, brought out some distinctive features. Many of the aggregates that appeared as highly electron-dense bodies (Plate 4b, lower left hand corner) now reveal themselves as residues of diatom walls (Plates 4e and 4f). It can be seen from the figures that these residues still retain some iron oxide coating and also reveal signs of disintegration of the siliceous structures. In Plate 5a, a remnant of a diatom shell is shown, revealing its highly porous surface, all of which remained coated and blocked with iron oxide and amorphous materials in the untreated sample. From the scale provided in the Plate, it can be seen that the size of the pore is of the order of 0.12 μ in diameter. These pores are instrumental in high polar liquid adsorption on these residues' surfaces. This is considered as the primary reason for the increase in surface area after oxalate treatment. This treatment also revealed that individual clay mineral particles dispersed after this treatment are extremely smaller, and most bigger particles represented only aggregates. This also provides a clue for the increase in surface area on oxalate treatment because of the release of more surface due to the dispersal of the finer particles.

In the case of the Henningkonglwa (Nagaland) sample, many aggregates in widely variable sizes with humus, amorphous materials and very small particles are observed, as shown in Plate 5b. Allophane and amorphous material with nostly humus were found to form discrete aggregates (Plate 5c). Presence of quartz (cf. mineralogy) was confirmed in Plate 5d. Quartz particles in this particle size fraction remained associated with each other and attracted particles finer than their size to their edges. Allophanes with specific shapes, extremely small globular allophanes (0.1μ in size) were found to form distinct aggregate in chains. Such aggregates are always found to be associated with some electron-dense particles almost of the same size and shape (Plate 5e). The occurrence of such allophanic chains is common in red and lateritic soils.

In Plate 6c, different aggregates of different sizes, with small mica particles, iron oxides, organic matter, and amorphous materials, are shown in the Palampur samples. As it occurs in soil (Naddi), the naturally occurring clay-organic complex will be clear from the two aggregates, one elongated and the other round shown in Plates 7c and 7d. Clays are normally held together in packages (domains) by a variety of agencies (organic matter, iron oxides and amorphous inorganic constituents), and these domains are bonded to form aggregates (Greenlands and Hayes1978).



PLATE 4: Electron micrographs for Jorhat samples (2-0.05 $\mu)$ JORHAT (2-0.5 μ

(a) Globular aggregates of very fine particles * 12720 (no treatment); (b) Circular, angular and irregular shaped aggregates * 20350 (Peroxide treated); (c) Globular allophane particles * 33580 (peroxide treated); (d) General view * 34200 (Peroxide-CBD-oxalate treated); (e) Iron -coated diatom shell * 21375 (Peroxide-CBD-oxalate treated); (f) Diatom shell uncoated with iron oxides * 21.75 (Peroxide-CBD-oxalate treated).



PLATE 5: Electron micrographs for Jorhat and Henningkonglwa samples (2-0.05 μ) JORHAT (2-0.05 μ) (a) Remnant of a diatom shell * 11850 (Peroxide-CBD-oxalate treated);

HENNINGKONGLWA

(b) Aggregates with humus, amorphous materials and small particles * 16280 (No treatment); (c) Humic substances with some amorphous materials * 20350 (No treatment); (d) pair of quartz particles * 27470 (No treatment); (e) Allophane chains * 20350 (No treatment); (f) Iron oxide nodules * 33580 (Peroxide treated).



PLATE 6: Electron micrographs for Henningkonglwa and Palampur samples (2-0.05 μ) HENNINGKONGLWA (2-0.05 μ)

(a) Amorphous materials forming aggregates * 20350 (20350 (Peroxide treated); (b) Mica flake coated and uncoated with silica gel like materials * 27470 (Peroxide-CBD-oxalate treated)

PALAMPUR (2-0.05 μ)

(c) Aggregates of small mica particles with amorphous materials, organic matter and iron oxides * 20350 (No treatment) ' (d) Aggregates consisting of highly degraded kaolinite with iron oxides and amorphous materials * 20350 (Peroxide treated) (e) Transformation of iron oxides to goethite particles * 42740 (Peroxide treated); (f) Chain of allophane crystals * 55965 (Peroxide treated).



PLATE 7: Electron micrographs for Palampur and Naddi samples (2-0.05 μ) PALAMPUR (2-0.05 μ) (a) General view * 27470 (peroxide-CBD-oxalate treated) ; (b) Mica flakes with clean surfaces *27470 (Peroxide-CBD-oxalate treated) NADDI (2-0.05 μ) (c) An elongated aggregate of organic matter amorphous material and mica_*12720 (No treatment); (d) A round

(c) An elongated aggregate of organic matter, amorphous material and mica *12720 (No treatment); (d) A round aggregate with amorphous materials in between particles *12720 (No treatment); (e) Mixed silicic acid and aluminium hydroxides *46200 (Peroxide treated); (f) Microaggregates of amorphous iron oxides with crystalline particles *12720 (Peroxide treated).

Historically, there was much interest in repulsive forces between soil particles, particularly in the clay fraction. This interest was understandable because if repulsive forces are dominant, soils become dispersed and are virtually unmanageable in the agronomic sense. However, the balance of attractive and repulsive forces determines whether the soil is flocculated or dispersed. By the mid-1950s, a swing towards studying the attractive forces between soil particles was well underway, and certain salient soil features began to be understood more widely.

In Chikballapur (red soil) samples, a typical aggregate of inorganic particles, oxides (electrondense zone in the middle) and some amorphous materials were observed in untreated samples (Plate 8c). Presence of highly dispersed amorphous substances was confirmed even as separate domains of their own (without either crystalline material or iron oxides) in this sample (Plate 8d). This is similar to Plate 227, as Beutelspacher and van der Marel (1968) reported. The material in Plate 4d is amorphous silica that appears as tiny sphere colloids forming small aggregates due to sonification. Such amorphous silica is common in red earths, latosols, gley soils and weathered sediments (Bhattacharyya 1980). Such amorphous silica also participates in aggregate formation (Plate 6a), which was observed in the peroxide-treated sample in Henningkonglwa.

In the untreated sample from Henningkonglwa, no separate aggregation of iron oxide/iron oxide nodules was observed. However, for organic matter removal, such aggregates were visible (Plate 5f). This suggests that aggregates of iron nodules in untreated samples remain associated with humus, giving an undifferentiated morphology to the aggregates.

The general morphological feature of the Palampur clay-organic complex after peroxide treatment is shown in Plate 6d. It is evident that it has been possible to get a much better degree of dispersion after this treatment, but the clay surface continues to be coated with amorphous materials. The kaolinite particles were better discernible from their hexagonal morphological features. The edges appeared smooth and rounded in many cases, possibly because of the coating on the surfaces and edges.

Besides iron nodules, microaggregates of amorphous and iron oxides were common in Palampur soil. Transfomation of iron oxides to crystalline goethite particles and association of such material into an irregularly shaped aggregate is presented in Plate 6e. In Palampur, globular allophane particles were found to form open aggregates with chain formation. This allophanic particle seems to be associated with iron oxide appearing as electron-dense areas in Plate 6f. A similar congregation of allophanic particles, which also seems to contain a coating of iron oxides, is presented in Plate 230 in the book by Beutelspacher and van der Marel (1968). Such globular allophanic particles are common in



PLATE 8: Electron micrographs for Naddi and Chikballapur samples (2-0.05 µ)

NADDI (2-0.05 μ)

(a) A big mica particle with clean surface * 12720 (Peroxide-CBD-oxalate treated) ; (b) An aggregate with relatively cleaned particles * 27470 (Peroxide-CBD-oxalate treated) ;

CHIKBALLAPUR (2-0.05 μ)

(c) Aggregates of particles with oxides and amorphous materials * 20350 (No treatment); (d) Dispersed amorphous materials * 20350 (No treatment); (e) Aggregates of hematite and globular allophanes * 20350 (Peroxide-treated) ; (f) Goethite particles * (Peroxide-treated).

volcanic ash soils. It is apparent from this study that such globular allophones can occur in widely variable genetic conditions. These observations were made possible only after organic matter removal, suggesting a possibility of iron oxide-organic matter-amorphous material association.

In the Naddi sample on peroxide treatment, crystalline particles were visible more clearly but remained in aggregated form. It was apparent that the majority of the crystalline particles were micaceous. The characteristic feature in this sample was the presence of microaggregates of amorphous materials, particularly the morphology of mixed silicic acid and aluminium hydroxides (Plate 7e). Such microaggregates were smaller than 1 μ size. Plate 233 in Beutelspacher and van der Marel's Book (1968) also explains the morphology of such mixed gels. Amorphous iron oxides associated with small crystalline particles forming microaggregates were also common. These aggregates were generally bigger (> 1 μ). Such aggregates are shown in Fig. 7f. In the Chikballapur sample, hematite particles (Plate 8e) and goethite particles (Plate 8f) were observed only after peroxide treatment. Thus, these iron oxides appear to have been associated with organic matter, and that association obscured their morphology. The presence of iron particles in these samples was expected, considering that these soils contain a very high amount of iron oxides.

Dithionite and oxalate treatments made the crystal morphology clearer (Plate 6b). Still, some gel-like coating was present on the mica particle; the treatments appear to have removed most of the coating in the Henningkonglwa sample.

A general view of cleaned clay particles (Palampur), mostly rounded kaolinite and mica, are shown in Plate 7a. These samples' treatment effects is clearer (Plate 7b). Though the surface of most mica particles was made free from coating materials, some particles showed a pitted appearance and also coating of amorphous material (lower left-hand corner, Plate 7b). Such was the observation with the Naddi sample also. In Plate 8a, a mica particle with a rather clean surface is presented.

Crystalline particles were found to form aggregates even in the absence of cementing materials. This is clear from the Plate 8b. Although some of the amorphous constituents do escape the treatments, the clearer portion of the micrograph shows the aggregates of individual particles. The effectiveness of oxalate treatment was more conspicuous in the Chikballapur sample. Kaolinite particles with rounded to subangular edges without or with very little surface coatings are visible. The sample also showed the presence of some mica flakes (Plate 9a).



PLATE 9: Electron micrographs for Chikballapur, Kohima and Tamanda samples (2-0.05 µ)

CHIKBALLAPUR (2-0.05 μ)

(a) Well dispersed mica and kaolinite particles * 27470 (Peroxide-CBD-oxalate treated); (b) Aggregates of particles * 27350 (No treatment); (c) Iron-coated diatomaceous shell * 20350 (Peroxide treated); (d) Globular microaggregates *20350 (Peroxide treated); (e) Kaolin and some mica particles *12270 (Peroxide-CBD-oxalate treated)

TAMANDA (2-0.05 μ)

(f) Aggregates of small particles with organic matter and amorphous materials * 20350 (No treatment).

In the Kohima sample, the aggregate shape varied from circular to elongated angular. The involvement of humus, amorphous and crystalline components was evident from electron microscopic studies. In Plate 9b, a circular aggregate and the portion of an angular aggregate are shown. The portion of the angular aggregate that has opened up reveals the cementing action of humus and amorphous materials between crystalline particles. In naturally occurring complexes, the particle forms aggregates of different shapes and sizes. It has been observed that particle sizes within a certain range tend to assemble in forming aggregates. In many of these samples, conspicuous segregation of aggregates consisting of particles within certain size limits were observed. The binding material, however, remaining similar. Aggregates formed by an assemblage of wide-ranging particles were relatively much less. Plate 9f is an example of an aggregate formed by wide-ranging particles in the Tamanda sample. In the same sample (Plate 10a), finer particles cluster together, forming spherical to semispherical aggregates mainly of kaolinite particles.

Peroxide treatment brought out the morphology of the inorganic material. Remnants of diatoms were visible, though still heavily coated with iron oxides (Plate 9c). In the same plate, highly electrondense aggregates of oval shape are also visible, indicating the involvement of iron oxide in cementation. Organic matter removal also revealed the morphology of other amorphous materials, forming irregular masses but very often globular microaggregates (plate 9d). In this sample, the clay mineral particles were so heavily coated with iron oxides and amorphous materials that their morphology Could rarely be seen. They appear only as large electron-dense aggregates. In peroxidised samples (Tamanda) elongate aggregates (Plate 10b) were quite common. Circular and globular microaggregates (Plate 10c) were also abundant and mainly had amorphous constituents. In elongated aggregates, the involvement of goethite particles was apparent. Some kaolinite particles at the edges show clear evidence of pitted Surface. In the rest of the area, the iron oxides' coating is so heavy that they appear only as electron-dense zones (Plate 10c),

CBD-Oxalate treatment helps remove non-crystalline substances that expose mineral surfaces. The crystalline component in the Kohima sample mainly consists of extremely small kaolinite particles and some mica particles (Plate 9e). The dominance of small kaolinite particles is the characteristic feature of this sample. The small kaolinite particles have subangular edges and tend to form an aggregate among themselves. Though they are extremely small, their surfaces do not show any



PLATE 10: Electron micrographs for Tamanda and Indore samples (2-0.05 $\mu)$ TAMANDA (2-0.05 $\mu)$

(a) Association of spherical to semi-spherical aggregates * 16280 (No treatment); (b) Elongated aggregates (*27470
(Peroxide-treated); (c) Circular and globular microaggregates * 16280 (Peroxide-treated); (d) Cleaned kaolinite particle with pitted surface * 46200 (Peroxide-CBD-oxalate-treated)

INDORE (2-0.05 µ)

(e) Oval to circular aggregate * 5700 (No treatment) ; (f) An elongated aggregate * 6920 (No treatment).
pitted appearance, whereas in the CBD-oxalate-treated sample from Tamanda (Plate 10d), the kaolinite particles have a pitted appearance showing the signs of degeneration. Very thin particles of kaolinite having rounded edges and the appearance of almost amorphous materials can be seen. In other words, kaolinite particles in various stages of degeneration were detectable in this sample after CBD-oxalate treatment.

The morphology of naturally occurring aggregates in the Indore sample is shown in Plates 10e, 10f and 11a. Oval to circular aggregates formed by compact arrangements of small spherical particles were common (Plate 10e). Sometimes, elongated particles tend to form an interwoven mass with humus and amorphous constituents forming elongated aggregates with relatively open structures (Plate 10f). Amorphous material or smectite also formed separate microaggregates, or such microaggregates of these components must have been separated due to the sonification of the sample and are discernible (Plate 11a). In smectite-dominant soils, elongated aggregates appeared to be a common occurrence. In the Siraguppa sample, such aggregates were formed by associating circular to globular microaggregates. Iron oxides and amorphous materials also seemed to be involved in the cementation of such macroaggregates in forming the bigger elongated aggregate (Plate 12a). Highly irregularly shaped aggregates joining together to form bigger ones were also common in this sample (Plate 12b). Similar observations were also made regarding the shape and size of naturally occurring aggregates in Nandyal samples. Microaggregates of smectite associated with iron oxides and amorphous materials seem to happen in higher proportion in this sample. One such macroaggregate is shown in Plate 12f.

On removal of organic matter, the elongated shape of the aggregate was no more conspicuous. The bigger aggregates split into small microaggregates and appeared as dispersed particles (Plates 11b and 11c). In forming aggregates, smectite forms an intimate association with amorphous material. In the upper right-hand corner of Plate 11d is shown as part of such a spherical aggregate, whereas the lower half of the plate depicts several such aggregates showing splitting. Closely examining the various regions showed the intimate mixing of electron-dense particles (having some shape), possibly smectite with less electron-dense and shapeless amorphous constituents. In the Siraguppa sample, on peroxide-treatment, the general morphology of the smectites was rather visible. As is normally the case, Smectite appeared as globular to circular aggregates mixed with iron oxides (Plate 12c). The long elongated aggregate was no longer visible. Smectites also form aggregates by stacking plate-shaped aggregates one above the other, cemented together by amorphous materials. One such aggregate is shown in Plate 12d. The Nandyal sample peroxide treatment revealed similar morphology of microaggregates of smectites and iron oxides as observed in the Siraguppa sample (Plate 13a). In this sample, hematite particle was found to form a distinct association.



PLATE 11: Electron micrographs for Indore samples (2-0.05 µ)

INDORE (2-0.05 µ)

(a) Microaggregates * 17100 (No treatment); (b) Microaggregates appearing as dispersed particles * 10175 (Peroxide-treated); (c) Microaggregates appearing as dispersed particles * 34200 (Peroxide-treated); (d) Smectite particles in association with amorphous materials *46200 (Peroxide-treated); (e) Aggregate of irregularly stacked smectite particles *46200 (Peroxide-CBD-oxalate- treated); (f) Thin flakes of mica * 46200 (Peroxide-CBD-oxalate- treated)



PLATE 12: Electron micrographs for Siraguppa and Nandyal samples (2-0.05 µ)

SIRAGUPPA (2-0.05 μ)

(a) Elongated aggregate * 14050 (No treatment); (b) Irregular shaped aggregates * 14050 (No treatment); (c) Smectite aggregated with iron oxides * 12270 (Peroxide-treated); (d) Irregular shaped micro aggregates * 30050 (No treatment); (e) Rounded micro aggregates of smectites * 12270 (Peroxide-CBD-oxalate-treated);

NADYAL (2-0.05 µ)

(f) Micro aggregates * 34200 (No treatment)



PLATE 13: Electron micrographs for Siraguppa and Nandyal samples (2-0.05 $\mu)$ NANDYAL (2-0.05 $\mu)$

(a) Smectite aggregate with hematite chain * 34200 (Peroxide-treated); (b) Spherical to irregular shaped smectite aggregates with amorphous iron oxides * 20350 (Peroxide-treated); (c) Aggregates of stacked smectites * 27470 (Peroxide-CBD-oxalate treated); (d) Micro aggregates of smectites * 34200 (Peroxide-CBD-oxalate treated)
CHIKBALLAPUR (2-0.05 μ)

(e) Kaolin aggregates with cementing materials * 27470 (No treatment); (f) Globular allophanic crystals forming chains * 33580 (No treatment)

Iron oxides are closely associated with smectite and form spherical to irregularly shaped aggregates, as shown in Plate 13b.

During the oxalate treatment, the morphology of the crystalline particle was visible. Mica particles could be easily identified from the morphology, and one such mica particle is shown in Plate 11f. Smectites, however, appeared as aggregates showing a specific pattern of irregularly stacked layers. This stacking pattern might have arisen due to sonification, which may help form clusters of extremely small smectite particles (Plate 11e). The morphology of smectite particles in the Siraguppa sample, on oxalate treatment, was quite different from that of the Indore sample. Here, the smectite appeared as rounded microaggregates of various sizes (Plate 12e). In the Nandyal sample, however, both types of morphology were detectable on oxalate treatment. Plate 13c shows morphology similar to that observed in the Indore sample, whereas Plate 13d shows morphology identical to that in the Siraguppa sample.

(b) <u>Finer fractions (<0.05 μ) of clay-organic complex with its various treatments</u>

For finer fractions, three samples were chosen one each from Alfisol (Chikballapur), Ultisol (Kohima) and Vertisol (Indore). In the Alfisol sample of Chikballapur, microaggregates are formed by the union of kaolinite particles with cementing material. These microaggregates were less than 0.5μ in diameter, and on storing after separation, they recombined from bigger aggregates of sizes above the size limit at which they were separated (Plate 13e). This indicates the existence of high residual surface attractive forces on this aggregate. Globular allophanes are common in this sample, forming chain-like arrangements by end-to-end attachment. Such chains are intercepted or combined to form open aggregates. It is curious that such an assemblage of allophane was found even in untreated samples. They also occurred separately without being aggregated with humus and/or other soil constituents, except that very often, some iron oxide appeared to remain associated with it (Plate 13f).

Two spherical aggregates occurring in the Kohima sample are shown in Plate 14e. In this sample, the finer particles formed smaller or bigger aggregates, which, on storing, tend to reunite. In Plate 14f, a large aggregate has developed after recombining microaggregates. A close examination of this micrograph indicates that the microaggregates are spherical. A chain of globular allophanic particle is also visible in the lower left-hand corner. Such allophanes are common in the Kohima sample and have the same aggregational characteristics as described earlier. The characteristic of aggregates of allophane is shown in Plate 15a. The association's properties in untreated samples are similar to those of Alfisols and Ultisols. The untreated aggregates in Vertisols (Indore) revealed a similar feature as that observed in coarser fractions except that here



PLATE 14: Electron micrographs for Chikballapur and Kohima samples (< 0.05 μ)

CHIKBALLAPUR (<0.05 μ)

(a) Free amorphous silica *12720 (Peroxide treated); (b) Association of free silica and amorphous iron oxides * 27470 (Peroxide treated); (c) Pattern of aggregate formation by very small kaolinite particles * 10175 (Peroxide-CBD-oxalate treated); (d) Hexagonal kaolinite particles with pitted surface * 56420 (Peroxide-CBD-oxalate treated)
KOHIMA (<0.05 μ)

(e) Association of spherical aggregates *20350 (No treatment); (f) Large aggregate formed by recombination of microaggregates * 10175 (No treatment).



PLATE 15: Electron micrographs for Kohima and Indore samples (< 0.05 μ) KOHIMA

(a) Aggregates of allophane * 55965 (No treatment); (b) Microaggregates with heavy iron oxides' coating * 42740 (Peroxide-treated); (c) Silicic acid gels * 20350 (Peroxide-treated); (d) Degraded kaolinite particles * 14050 (Peroxide-CBD-

oxalate-treated);

INDORE

(e) Aggregates of smectite particles * 20350 (No treatment); (f) Typical iron oxide -coated aggregate * 27350 (Peroxide-

treated)

the sizes are smaller. The small aggregates appear as irregular assemblage of extremely fine particles. A large part of the material appears more like amorphous constituents (Plate 15e).

The morphology of the amorphous constituents became clear only after the removal of organic matter. As indicated earlier, this is obviously due to the closer association of these two constituents. Chikballapur showed the presence of free amorphous silica (Plate 14a). Beutalspacher and van der Marel (1968) presented a similar electron micrograph of amorphous silica. This plate shows that such silica is not always involved in aggregate formation with all soil constituents, though it may have very high surface reactivity. However, there is evidence that such silica and iron oxide particles form a preferential association of various shapes and sizes. Such association of free silica and amorphous iron oxides (electron-dense globular particles) is shown in Plate 14b. In the Kohima sample, after organic matter removal, the microaggregates were found to form, mainly by a combination of amorphous iron oxides and crystalline minerals. The iron oxides also formed separate aggregates besides binding other particles (Plate 15b). The occurrence of free amorphous silica was also found in this sample (Plate 15c). The high porosity and irregular shape of the dried sample is noticeable. The crystallinity of the particles was revealed somewhat better when samples were treated with hydrogen peroxide. Even when organic matter was removed, the particles were found to be coated with iron oxides to form aggregate. One such typical aggregate is shown in Plate 15f, and silica-alumina gels appeared to be common in this sample from Indore. Such mixed gels with smectite particles are shown in Plate 16a. The mixed gels appeared to be transforming into definite shapes, possibly indicating crystallization into a mineral form. Material in such stages of transformation was also detectable in the sample. In plate 16b, such a situation is presented. This may also represent the break-down of already neoformed micro-crystalline particles. On oxalate treatment, most of the aggregates dispersed into individual particles but remained attached to each other through edges. This association also gives the appearance of pseudo-aggregates (Plate 14c). However, the individual particles were rather clearly visible and were fine kaolin particles. These particles were found to have a pitted appearance at high magnification with rounded edges. This is a clear sign of a high degree of weathering of kaolinite particles themselves (Plate 14d). Some smaller particles are found to have almost lost their hexagonal morphology and appear as irregular masses. In the Kohima sample, although oxalate treatment revealed the particles' morphology rather clearly, many particles remained in macroaggregate form, and there were clear signs that all amorphous materials were not removed. The dispersed individual particles were of extremely small size ($<0.1 \mu$), whereas the size of aggregates varied from roughly $0.2 - 0.5 \mu$ (Plate 15d). Most of these particles were kaolinite, and thin mica flakes were also visible. Oxalate treatment led to the dispersion of the clay particles in the Indore sample. The dominant mineral, smectite, appeared as an extremely tiny particle



PLATE 16: Electron micrographs for Indore samples (< 0.05 μ) INDORE (<0.05 μ)

(a) Silica-alumina gels with smectite particles * 46200 (Peroxide-treated); (b) Transformation of mixed gels * 20350 (Peroxide-treated); (c) Highly dispersed smectites * 10175 (Peroxide-CBD-oxalate-treated); (d) Big mica particle * 12720 (Peroxide-CBD-oxalate-treated).

having no specific shape. However, they also formed microaggregates, which appear as electron-dense aggregates in Plate 16c. Oxalate treatment removed most of the amorphous material from this sample. The surface of the mica particle present in the sample appeared rather clear (Plate 16d).

Electron microscopic examination revealed that hydrous oxides and allophane acted as strong adsorbents for organic matter. Clay surface also adsorbed organic matter, but possibly to a lesser extent. Therefore, the involvement of all these components is quite obvious in forming a naturally occurring clay-organic complex. What is known about the behaviour of humic and fulvic materials at clay surfaces suggests that they do not create a surface coating. The dominant mechanism of their association with clays appears to be through complexing with calcium, iron or, probably most importantly, aluminium iron at the clay surface (Greenland 1971). They only become associated with siloxane surfaces by interacting with exchangeable ions or precipitating hydroxyl polymers at the surface. They are not adsorbed in the interlayers of expanding lattice minerals, except for fulvic materials of exceptionally low molecular size, which have been shown to be able to penetrate the interlayer space of aluminium montmorillonite in extremely acid (pH 2-5) conditions (Schnitzer 1968), Greenland and Hayes (1978) has also observed that hydrous oxides of iron and aluminium in soils are often associated with humic and fulvic materials. The adsorption mechanism is probably ligand exchange with surface hydroxyls. The strength of association suggests that several carboxyl groups may be involved, making it difficult to displace the humic group.

The electronmicroscopic studies further show that Fe-oxides exist as separate micronodules apart from remaining associated with crystalline particles. Such observation was also made by Kamf (1981) with kaolinite dominant clays. Besides iron oxides, amorphous materials were also observed to remain as separate entities in these samples, more so when peroxide-treatment was ensured to separate organic constituents. This suggests that although these materials are coated on the crystalline component of the naturally occurring clay-organic complex, the association is observed more with organic matter, amorphous constituents and iron oxides. As these materials have a tremendous surface area, their removal naturally decreases a specific surface area in most cases. This was observed in peroxide-treated samples of Henningkonglwa, Palampur, Bentlu, Mohitnagar, Chikballapur, Tamanda, and Karnal where surface area values decreased appreciably. The samples where the treatments increased the surface area had either newly exposed surfaces of some constituents (e.g., diatoms) or minerals with relatively more surface area (for vermiculite or smectitic clay minerals). The examples of the first case were Jorhat and Kohima, while the latter were Karnal and Naddi samples. It should be mentionedhere that while examining peroxide-treated samples, left over organic materials were observed, which were mostly present in a complex combination with iron oxides or amorphous material. The further treatment of the samples with CBD-oxalate removed those organic matters. This is why the peroxide-treated samples

gave absorption band in the 1600-1700 cm-1 region due to the residual OM in the I.R. absorption spectra, which subsequently disappeared or almost flattened in CBD-oxalate-treated samples. A close look at the electro-micrographs after peroxide-CBD-oxalate treatments reveals that some iron oxide coatings with amorphous materials remain in the samples. It indicates that these amorphous-ferroalumino-silicates are part of the soil system, and they have different degrees of stability and, hence, solubility in oxalate reagents. They were in the soils earlier and were not formed as the consequences of the treatments as observed with acid treatment, dissolving mineral constituents and forming amorphous materials. The actual morphology of the clay minerals is obtained only after these treatments. Without this, pseudomorphology often leads to erroneous conclusions. While examining the microaggregates of kaolin minerals with hematite in clay samples of Terra-Rosa soils from which free iron oxides were removed with a buffered dithionite, Kitagawa (1983) found that very fine particles of hematite were still present only where the part of the hexagonal plate of kaolin minerals overlapped, and were not found in other parts. Accordingly, he stated that hematite could act as a cementing material on forming stable aggregates in these soils. Deshpande and his associates (1968) observed gel-like materials even after buffered dithionite treatments in the electron micrographs. To get the particles cleaned, those materials could be removed only after 5% Na2CO3 treatment. In the present investigation, however, even after CBD and one oxalate treatment, completely clean surfaces of minerals could not be obtained, as already mentioned.

Coatings of hydrous oxides are often reported to be present on the surfaces of clay minerals. Very little direct evidence of the presence of such coatings has been reported. However, electron micrographs of particles from South Australian soil have shown these clays to be coated with a substantial silicious crust, probably of silica-alumina similar to poorly ordered "illite" (Wada and Greenland 1970). The rather frequently made suggestion that the kaolinite particles, which form the main constituent of the clay fraction of many tropical soils, are coated with iron oxides to give the soils their red colour is probably not always correct. Electron micrographs show iron oxide to be present in many such soils as small, discrete particles (probably ferrihydrite). Although coatings of iron hydroxide can be precipitated onto kaolinite particles under suitable (acid) conditions (Greenland 1975), similar features are not normally seen in soil clays, although in some hydromorphic soils, as reported by Habibullah et al. (1971), where iron hydroxides may be seasonally dissolved under reducing conditions and reprecipitated under oxidizing conditions precipitates of iron hydroxides may envelope clay particles. In this study, such discrete iron oxide (electron-dense) particles were found to coat the surfaces of kaolinite particles in the Kohima sample (Plate 15b).

Several studies of the weathering of biotite have shown that iron is expelled from the mineral lattice during the alteration process and appears as hydrous oxide coating on the surfaces of the hydrobiotite or vermiculite particles formed (Roth et al. 1967, 1969; Farmer et al. 1971). There is some

evidence that in soils containing vermiculite, these hydrous iron oxides persist as interlayer or surface coatings since treatment with dithionite to remove them increases the negative charge. In several other soils, including a wide variety of red, tropical soils, removing iron oxides did not increase negative charge (Deshpande et al. 1964). In the Palampur sample, removing organic matter resulted in only a slight change in the CEC values. Such was the case with Jorhat samples also. However, there was a greater decrease in CEC values when CBD-oxalate treatments were given to these samples. The Kohima sample changed slightly; so far, the CEC values are concerned with different treatments. As the removal of the surface coating did not change the charge characteristics, it indicates that the crust and the underlying material are similar in composition. Perhaps this explanation holds for Kohima samples.

10. <u>Content of crystalline constituents (2-0.05 μ) by X-ray diffraction</u> <u>analysis</u>

(i) Interpretation of X-ray diffractograms

The diagnostic lattice spacings (Å) observed in the X-ray diffractograms are given in Appendix I.

The X-ray diffractograms of cleaned clay (< 2 μ) of Indore black soils are given in Fig.20. The clay was dominated by smectite. The diffraction peak at 15.24 Å in the Mg-saturated sample shifted to 19.68 Å, and the second order peak at 9.66 Å appeared on qlycerolation. This was the confirmation of the presence of smectite. The diffraction peaks around 14.0, 7.2, 4.7 and 3.5 Å in all the treatments confirmed the presence of chlorite, while the peaks at 7.2 and 3.5 Å left on HCl treatment of the sample indicated the presence of kaolinite. The characteristic peaks of mica at 10.1, 5.0 and 3.3 Å confirmed its presence. The peaks at 4.27 and 3.3 Å indicated quartz's presence.

In the case of the Siraguppa sample, the X-ray diffractograms are given in Fig.21. The diffraction peaks at 18.6 and 9.4 Å in the Mg-glycerolated sample confirmed the smectite's presence. The presence of kaolinite was confirmed by peaks at 7.1 and 3.5 Å, which are absent in the K-saturated 550°C heated sample but appeared as weak peaks in the treated sample. The peaks for chlorite at 14.2, 7.2, 4.7 and 3.5 Å in all treatments were also observed.

In the Nandyal sample, the dominance of smectite was confirmed by strong reflection at 15.92 Å in the Mg saturated sample, which shifted to 19.0 on glycerolation. The presence of 7.2 and 3.5 Å peak in all the treatments, except in the sample neated to 550°C after K saturation, confirmed kaolinite's presence. Lines at 10.52 and 4.98 Å confirmed the presence of mica, while the presence of quartz was confirmed by the peaks at 4.27 and 3.2 Å (Fig. 22). In the case of Mohitnagar sample, the strong reflections at 10.1, 5.0 and 3.3 Å confirmed the presence of mica. The K saturation and subsequent

heating of the sample confirmed the presence of mica-vermiculite interstratifications in this sample. Peaks at 7.2 and 3.5 Å confirmed kaolinite as one of the minerals in this sample. 4.27 and 3.2 Å peaks confirmed the presence of quartz (Fig.23). Chlorite peaks at 14.30, 7.1, 4.7 and 3.5 Å were also observed in this sample.

In Karnal samples, mica (10.1, 5.0 and 3.3 Å), kaolinite (7.2 and 3.5 Å), vermiculite (14.2 Å) and quartz (4.27 and 3.3 Å) were the minerals present. Vermiculite was confirmed by the shift of 14 Å peak to 12 Å on K-saturation (Fig.24).

The X-ray diffractograms (Fig.25) show the dominance of kaolinite in the Chikballapur (Bangalore red soil) sample. The peaks at 7.2 and 3.6 Å confirmed the presence of kaolinite, while 10.4, 5.0 and 3.3 Å characterised mica as the other clay mineral.



Figure 20. X-ray diffractograms of Indore soil clay (2-0.05 µ)



Figure 21. X-ray diffractograms of Siraguppa soil clay (2-0.05 $\mu)$







Figure 23. X-ray diffractograms of Mohitnagar soil clay (2-0.05 $\mu)$



Figure 24. X-ray diffractograms of Karnal soil clay (2-0.05 µ)



Figure 25. X-ray diffractograms of Chikballapur soil clay (2-0.05 $\mu)$

Mica was the dominant clay mineral in the Bentlu sample with 10.2, 5.0 and 3.3 Å basal spacings. The 7.2 and 3.6 Å peaks confirmed Kaolinite, and their absence in K-saturated samples confirmed the presence of mica-vermiculite type of interstratification. Peaks at 14.2, 7.2, 4.7 and 3.5 Å in all the treatments indicated the presence of chlorite. Quartz was also present in this sample (4.3 and 3.24 Å) (Fig.26).

In the X-ray diffractograms of Naddi samples (Fig.27), the presence of 14.3, 7.22, 4.78 and 3.59 Å reflections showed the occurrence of 14 Å mineral in this sample. The intensity of 14 Å mineral was reduced on glycerolation, giving rise to a small reflection at 18.8 Å, suggesting the presence of the small amount of smectite. The sharp 10 Å reflections also showed an asymmetric nature toward the low angle side owing to the presence of interstratified materials. The reflections at 10, 5.0 and 3.3 Å showed the dominance of mica. The intensity of the reflections from micaceous minerals was increased on K-saturation owing to the assemblage of the collapsed interstratified materials. Sharp reflections at 7.2 and 3.5 Å showed the presence of a fairly high amount of kaolinite, which was confimed by their presence in the HCl-treated sample. This was necessary to distinguish between the first and second-order diffraction maxima from the small second and third-order reflection of 14 Å components, which appeared at 7.20 and 3.59 Å in the sample heated to 550°C. The 14 Å components were dissolved in HCl; therefore, these 7.22 and 3.59 Å reflections in the HCl-treated sample were attributed to kaolinite. A small amount of quartz (4.26 and 3.36 Å) was also present.

X-ray diffractograms of the Palampur sample revealed that chlorite, a 10 Å mineral (mica), kaolinite, interstratifications of mica-chlorite and a small amount of quartz were present (Fig. 28). Presence of chlorite is ascertained by the presence of a peak at 14.2 Å, second and third order reflections were observed at 7.1 and 4.7 Å along with high reflection at 3.5 Å. Peaks observed at 10.2, 5.0 and 3.3 Å were due to the presence of mica. The sharp 10.2 Å reflection was slightly asymmetrical towards the low angle side, with a tail suggesting a mixed-layer mineral with an expanding lattice component or 14 Å layers. A small peak at 11.9 Å in the Mg-saturated sample, which was responsible for the asymmetric nature of 10 Å reflection (towards low angle side) and 14 Å reflection. Since these peaks persisted even on heating, they were attributed to a mica-chlorite interstratified mineral. Sharp reflections at 7.15 and 3.56 Å remained unaffected on heating up to 300°C but vanished on heating the samples to 550°C. Furthermore, their presence in the HCI-treated sample confirmed the presence of kaolinite. Weak reflection at 4.23 and 3.37 Å confirmed the presence of quartz in this sample.



Figure 26. X-ray diffractograms of Bentlu soil clay (2-0.05 μ)



Figure 27. X-ray diffractograms of Naddi soil clay (2-0.05 $\mu)$



Figure 28. X-ray diffractograms of Palampur soil clay (2-0.05 $\mu)$

In Kohima samples, kaolinite (7.14 and 3.54 Å), mica (10, 5.01 and 3.37 Å), chlorite (14.68, 7.17, 4.78 and 3.54 Å) and quartz were present. Besides, there were random interstratifications of mica-vermiculite, as revealed from thorough scrutiny of the different diffractograms (Fig. 29). The peaks in between 14 and 10 Å started collapsing on K saturation. The collapsing continued with heating to 300^oC, and at 550^oC, it collapsed to 10 Å. This sample has a small peak at 14 Å mineral (possibly chlorite). Similar was the mineralogy of Jorhat samples, except that quartz is absent in this sample (Fig.30).

Tamanda, Henningkonglwa, and Katwa samples (Fig. 31, 32, 33) also have similar mineralogy as the Kohima sample with few variations. In Katwa samples, a small amount of smectite was detected, but quartz was absent. In Henningkonglwa samples, quartz was present. In both cases, the interstratified mineral present was a mica-vermiculite type. In the Tamanda sample, interstratification was mica-chlorite type, as revealed by a 12 Å peak in the K-saturated sample heated up to 550°C.

(ii) <u>Semiquantitative distribution of clay minerals</u>

The result of the semiquantitative analysis of clay minerals is presented in table 20.

All three black soils had smectite as the dominant mineral. In Indore, mica was also present (30%) appreciably. The chlorite content was similar in the Indore and Siraguppa samples (15% and 19%, respectively). The latter one, however, did not contain mica. Nandyal had a similar quantity concerning mica (7%), kaolinite (6%), and traces of quartz. Quartz was not found in the Indore and Siraguppa samples.

Henningkonglwa samples were found to be dominated by mica (42%), kaolinite (24%) and interstratified minerals (25%), which are almost similar in quantity. Chlorite (6%) and quartz (3%) were the other minerals.

Palampur, Naddi, Kohlma, Bentlu and Mohitnagar had similar mineralogical makeup, except a trace of smectite was present in the Naddi sample. Interstratified minerals (40%) were the maximum quantity in the Kohima sample, which also had quartz in quite an appreciable amount (10%). In Naddi, Bentlu, Palampur and Mohitnagar, mica was the dominant mineral ranging from 40-58%. Kaolinite was also present in appreciable amounts in Naddi (23%), Kohima (25%) and Bentlu (25%).

Chikballapur and Tamanda samples were dominant in kaolinite (77% and 44% respectively). Mica was the second mineral in Chikballapur (23%). Tamanda had chlorite (6%), interstratified minerals (20%), mica (25%) and quartz (5%).



Figure 29. X-ray diffractograms of Kohima soil clay (2-0.05 µ)



Figure 30. X-ray diffractograms of Jorhat soil clay (2-0.05 μ)



Figure 31. X-ray diffractograms of Tamanda soil clay (2-0.05 $\mu)$



Figure 32. X-ray diffractograms of Henningkonglwa soil clay (2-0.05 $\mu)$



Figure 33. X-ray diffractograms of Katwa soil clay (2-0.05 µ)

Sl.	Soils	Mineral Composition (%)							
No.		Smectite	Vermiculite	Chlorite	Interstratified minerals	Mica	Kaolinite	Quartz	
1.	Bentlu			7	8	56	25	traces	
2.	Mohitnagar	-	-	17	29	40	10	4	
3.	Karnal		4			84	11	traces	
4.	Katwa	9		19	13	47	12		
5.	Jorhat			19	17	33	31		
6.	Henningkonglwa			6	25	42	24	3	
7.	Palampur			16	6	54	12	traces	
8.	Naddi	Traces		10	4	58	23	Traces	
9.	Chikballapur					23	77		
10	Indore	52		15		30	3		
1	Nandyal	87				7	6	traces	
12	Siraguppa	70		19		ł	11		
1.	Kohima			10	40	15	25	10	
14	Tamanda			6	20	25	44	5	

Table 20. Mineralogy of	the peroxide-CBD-oxalate treated	complex
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Karnal and Katwa samples had mica as the dominant mineral (84% and 47% respectively). Karnal samples contained vermiculite in small quantities (4%) with 11% kaolinite and traces of quartz. Katwa samples contained 9% smectite, 19% chlorite, 13% interstratified minerals and 12% kaolinite. Jorhat samples had almost similar amounts of mica (33%) and kaolinite (31%). Chlorite (19%) and intergrade minerals (17%) were also present in this sample. Thus, based on X-ray analysis, clay minerals were detected mainly in the complex. Chemical analysis, however, indicated the presence of some primary minerals, particularly Ca-bearing minerals. However, Xs-ray studies failed to detect any such minerals, suggesting that their content must be below the limit of detection by this technique under the conditions of the experiment.

5. SUMMARY AND CONCLUSION

Based on the organic matter content and clay content 14 soil samples were selected from four soil groups namely Entisols (Bentlu, Mohitnagar, Karnal, Katwa and Jorhat), Alfisols (Henningkonglwa, Palampur, Naddi and Chikballapur), Vertisols (Indore, Siraguppa and Nandyal), and Ultisols (Kohima and Tamanda). To screen the existing methods for extracting amorphous constituents, the soils were treated with 0.5N NaOH, 5% Na₂CO₃ hot and cold) and 0.3M ammonium oxalate. Three pure minerals, kaolinite, mica, and montmorillonite, were also tested to determine the efficacy of different extractants. Out of the three extractants, oxalate dissolved less SiO₂ and Al₂O₃ from the minerals. This indicated that this extractant dissolved SiO₂ and Al2O3 primarily from non-crystalline counterparts and, therefore, was more effective in characterizing them. When comparing the dissolved constituents, 0.5N NaOH and 5% Na2CO3 were dissolved in higher amounts. Such observations were true in the case of soils as well. This led to the selection of ammonium oxalate as the suitable extractant for characterizing amorphous constituents in this investigation.

Soils were treated with NaOH-Na-hexametaphosphate, and organic matter was collected. From this organic matter, humic acid was separated, purified and characterised concerning the following properties:

1) <u>Carbon content</u>

The carbon content of the humic acids ranged from 31.71-55.29%. Alfisols were found to have relatively lower carbon content in humic acid, while Entisols and Vertisols had relatively higher values. Humic acids from Ultisols were found to have values between Vertisols and Entisols.

2) <u>Nitrogen content</u>

The nitrogen content of the humic acids ranged from 2.23-4.82%. Entisols and Vertisols samples contained relatively higher amounts of N than Alfisols and Ultisols.

3) <u>C:N ratio</u>

Results indicated a wider variation in the C:N ratio of humic acid in Entisols and Alfisols than in Vertisols and Ultisols. The trend showed an increase in this ratio in the order: Vertisol > Ultisol > Alfisol > Entisol.

4) <u>E₄: E₆ ratio</u>

Results showed that leaving aside the Ultisol of Kohima, the Vertisols and Ultisols had relatively wider E₄:E₆ ratios, suggesting a lower degree of aromatization. Thus, lower degree of aromatization is associated with high degree of soil weathering. Karnal, Jorhat (Entisols), Chikballapur (Alfisols) and Kohima (Ultisols) had narrow ratios.

5) <u>Infrared studies</u>

The aliphatic-CH absorption band (2900 cm⁻¹) was well delineated in the Nandyal sample out of the 14 humic acid samples. This band was missing in Naddi and Tamanda samples. Aromatic C=O groups were more in Karnal, Jorhat (Entisols), Chikballapur (Alfisols) and Kohima (Ultisols), as evidenced by the stronger band observed at 1640 cm⁻¹. It suggested that these four samples contained humic acids, which were more aromatised than others. $E_4:E_6$ ratio data also supported this conclusion.

Soils were sonified with distilled water, and the clay-organic complex was separated following Stoke's law. The coarse fraction $(2-0.05 \ \mu)$ was collected after removing the 0.05 μ fraction. The fine fraction (< 0.05 μ) of a few selected samples (Chikballapur, Indore and Kohima) was collected from the suspension using a membrane filter for the electron-microscopic work. The complexes thus collected were given two treatments viz. (i) hydrogen peroxide (30%) for removal of organic matter, and (ii) hydrogen peroxide-CBD –oxalate treatments for removing organic matter, free oxides and amorphous materials. The following studies were conducted with the clay-organic complex (untreated), peroxide-treated coarse fraction (PTCF), and peroxide-CBD-oxalated-treated coarse fraction (POTCF).

(1) <u>Organic matter content (%)</u>

Organic matter content (%) was estimated in the clay-organic complex. Among the Entisols, Mohitnagar and Jorhat had relatively higher organic matter. Organic matter content was higher in the Palampur, Henningkonglwa and Naddi samples (Alfisols). Among Ultisols, Kohima had the maximum content of organic matter. The Vertisol complexes generally had lower organic matter values in the size fraction studied. Relatively higher organic matter content in the Mohitnagar sample is due to the enrichment of humus coming as washings from higher altitudes. In the case of Palampur, Henningkonglwa and Naddi samples, the favourable vegetation and climatic conditions probably resulted in a slow humification process, leading to a higher organic matter association in the naturally occurring clay-organic complex. In Kohima, such reason holds good due to the vegetation cover and high rainfall in this region. The sample from mountain and hilly tracts observed high organic matter content.

(2) <u>Total nitrogen content (%)</u>

Siraguppa (Vertisol), Mohitnagar, Karnal and Jorhat samples (Entisols) had a higher total N content in the complexes. Organic matter removal resulted in the loss of N in all the samples. The N content decreased in 6 samples and remained unchanged in 8 samples when organic matter, free oxide and amorphous materials were removed. Interestingly, even when organic matter was removed, N was associated with the samples. This was also observed in the cleaned samples. As this N cannot come except from organic matter, it suggests that organic matter is intimately associated with the mineral constituents; the treatments, therefore, failed to remove them completely. Electron microscopic observations further confirmed the presence of residual organic matter in most PTCF and POTCF samples. (3) Total surface area (m^2/g)

Surface area values were higher in the Vertisols among all the four groups of soils studied. In the case (except in Naddi), the removal of organic matter resulted in a decrease in Bentlu, Mohitnagar, Karnal (Entisols), Henningkonglwa, Palampur, Chikballapur (Alfisols) and in all the three Vertisols. When CBD-oxalate treatment was given on a peroxidised sample, the surface area values generally decreased. This is because of the removal of the materials (oxide and allophanic materials) having a high surface area. The surface area values increased in Karnal, Katwa, Kohima, Jorhat and Naddi samples. The reasons are different in different samples. Karnal, Naddi, and Katwa clay contained smectite and vermiculite. The removal of the coatings from these minerals has increased the surface area value. In Kohima and Jorhat samples, the diatoms with their residual porous, silicious structures (as evidenced in the electron micrographs) increased the surface area when the oxidic coatings were removed.

(4) <u>Cation exchange capacity (CEC, me/100 g)</u>

Indore, Siraguppa (Vertisols), Mohitnagar, Karnal (Entisols), Henningkonglwa and Chikballapur (Alfisols) samples had relatively higher CEC values. In general, Ultisols registered lower values of CEC in the naturally occurring clay-organic complexes. The CEC values increased after peroxide treatment in Nandyal, Henningkonglwa, Palampur, Naddi, Tamanda and Katwa samples. The fall in CEC values in other samples after peroxidation points to the fact that the reactivation of exchange sites of inorganic components could not make up for the loss of exchange sites due to the removal of organic matter. Hence, the result is a fall in total CEC values. Indore, Kohima, Bentlu, Mohitnagar, Chikballapur and Karnal samples were examples. In Jorhat and Palampur samples, there were insignificant changes in CEC value compared to peroxidised samples. In such complexes, organic matter and amorphous association were more common. The increase in CEC values may be due to high exposure to CEC clay minerals. Removal of organic matter, free oxides and amorphous materials resulted in a decrease in CEC values in all the samples.

(5) K-fixation capacity

Higher K fixation capacity was observed in the naturally occurring clay-organic complex of the three Vertisols. Among the other three groups of soils, Karnal (Entisol), Henningkonglwa and Chikballapur (Alfisols) samples registered appreciable fixation by the untreated complex. Removal of organic matter increased fixation capacity. Fixation of K showed a further increase when free iron oxides and amorphous constituents were also removed from peroxidized samples except in Nandyal and Siraguppa, which were exceptions. The results indicate that the coatings of organic matter, free iron oxides and amorphous materials block the fixation sites, which are subsequently exposed owing to the treatments. The higher difference in K fixation capacity between peroxidized and untreated samples than observed between peroxidized and cleaned samples suggests that organic matter has a higher degree of blocking effect. In other words, clay-organic matter association is more effective in blocking fixation sites in these cases. The examples were Bentlu, Karnal, Katwa and Jorhat samples (Entisols), and Nandyal and Siraguppa samples (Vertisols). The situation was exactly reversed in all the Alfisols,

Mohitnagar (Entisol) and Indore (Vertisol) samples, where clay-amorphous/iron oxides association was more effective in blocking fixation sites. The decrease in K-fixation values after removing oxides and amorphous materials (viz. Nandyal and Siraguppa) might well suggest a possibility of association of amorphous material with potassium, which led to a fall in fixation values when those materials were removed.

(6) <u>Infrared studies</u>

The infrared studies of the complex with different treatments revealed quite interesting observations. surfaces of the crystalline component were cleaned, the shoulder bands around -OH absorption bands gradually disappeared, which may either be due to the restoration of symmetry of OH vibration in the silicate crystals or may be due to the decrease in the content of functional groups. The kaolinite dominant samples (Chikballapur, Tamanda and Jorhat) gradually showed an increased intensity of 3680 cm-1 band as the surfaces became cleaner and cleaner. This is apparent because edge-OH groups of kaolinites play a dominant role in these soils. As the intensity increases on removing OM and free oxides, it indicates that organic matter and amorphous oxides are bonded through these -OH groups.

The increased intensity of the structural -OH band around 3400 cm⁻¹ in most of the peroxide-treated samples may well be due to the increase in the relative proportion of the amorphous oxides, the removal of which, however, subsequently decreased the intensity of this band. The examples were Indore, Nandyal (Vertisols, Karnal (Entisol), Henningkonglwa, Palampur (Alfisols) and Kohima (Ultisol). The stepwise decrease in the intensity of this band suggests the gradual loss of the complex-forming functional groups. In Mohitnagar, Katwa and Jorhat (Entisols) and Tamanda (Ultisol), no change in band intensity was observed in the peroxide-treated samples. This indicated that the organic matter existed more as free form than formed complex through OH-functional groups. During electron microscopic studies, the occurrence of free organic matter was noted. However, CBD-oxalate treatment decreased the intensity. This was due to the removal of amorphous oxides and the organic matter associated with these oxides. Electron microscopic observations also supported this explanation.

Organic matter removal in all the samples decreased the 1600 cm⁻¹ band intensity except in Karnal, Indore and Siraguppa. A decrease is expected because hydrogen peroxide and CBD-oxalate treatments have largely removed the C=O functional groups responsible for this band. The complete disappearance of the 1430 cm⁻¹ band in peroxide-treated samples from Mohitnagar, Henningkonglwa and Indore also speaks for the argument mentioned above. In Bentlu, Karnal, Katwa, Jorhat, Palampur, Nandyal and Kohima, this band appeared with decreased intensity or as shoulders, indicating the removal of organic matter.

Removal of organic matter resulted in shifting the 1000 cm⁻¹ band to a higher frequency; this shift was more in Henningkonglwa and Nandyal samples and much less in Siraguppa and Kohima samples. It indicates that functional groups of organic matter are possibly more involved in complex formation for the Henningkonglwa and Nandyal samples. CBD-oxalate treatment resulted in a higher shift in Siraguppa and Kohima samples, suggesting a greater association of oxides and amorphous materials. This treatment could only slightly shift in Henningkonglwa and Nandyal samples. Except for these four samples, the other samples generally suffered a shift in this band towards lower frequency.

The 960-550 cm-1 bands became sharp and well pronounced when organic matter was removed in Indore, Karnal, Chikballapur, Palampur, Nandyal and Kohima samples. This indicates the involvement of organic matter in complex formation through its functional groups. CBD-oxalate treatment could not remove all the extraneous materials from the mineral surface. The involvement of the inorganic constituents with organic matter in complex formation has also been indicated in electromicroscopic examinations. Peroxide could oxidise the organic matter more efficiently in Bentlu, Katwa, Jorhat, Henningkonglwa, Naddi and Tamanda samples, as evidenced by the relatively weak bands registered in this region.

(7) Total chemical composition

The complex's ignition loss decreased gradually as organic matter, iron oxides, and amorphous materials were removed stepwise. As organic matter does not contain silica, removal of this should show an increased value of total silica. Such was the observation in all the samples except in Naddi, where the SiO_2 content decreased. This was due to the removal of some silica by peroxide treatment during organic matter removal. Both increases and decreases in SiO2 content were also obtained in CBD-oxalate treated samples. In cases where the material removed had a higher percentage of SiO_2 than the residual crystalline material, the rate of SiO_2 decreased and <u>vice-versa</u>.

Removal of organic matter resulted in the reduction of the total Fe₂O₃ content of the complex, showing that peroxide treatment removed some of the free iron oxides. Such observation in all these samples, especially in Mohitnagar and Karnal, indicates Fe-organic matter association. In other samples, no change in Fe₂O₃ value was observed when organic matter was removed. This suggests that these samples have no separate complex of organic matter with iron. As expected, CBD-oxalate treatment resulted in an overall decrease in iron oxide content except in a few samples where the reduction was insignificant. The content of alumina was also observed to decrease or increase due to the removal of organic matter. As mentioned earlier, like silica, some alumina seemed to be solubilized by hydrogen peroxide, leading to a decrease in the content of Al₂O₃. Besides, the CBD-oxalate treatment increased Al₂O₃ content in all the samples with a few exceptions. Very high values of CaO and MgO were found in the clay-organic complex. This indicates the importance of these aggregates in retaining nutrient cations and releasing them to the plants as and when required. These high values follow these complexes' very high exchange capacities. This was true even for soils containing kaolinite and mica. The calcium and magnesium oxide values decreased when organic matter was removed from the sample. This indicates the involvement of Ca and Mg in forming the clay-organic complex. The participation of these divalent cations in creating bridges between the amorphous and crystalline constituents and the functional groups of organic matter is a well-known fact. Clays separated by the established procedure do not generally contain such high quantities of CaO and MgO as found in this

study in the cleaned sample. This indicates that highly insoluble Ca-minerals like apatites, carbonates, and feldspars are constituents of these complexes in various proportions. In general, the total potash content of the complex increased when organic matter was removed.

Henningkonglwa and Katwa samples were the two exceptions. This was explained because organic matter forms the coating on the fixation sites for K in the crystalline minerals. Allophanes also fix K. in that case, the increase may also be due to the removal of organic matter in association with amorphous materials. Such associations were common in these naturally occurring clay-organic complexes. In some of the Entisol, Alfisol, and three Vertisol samples, CBD- oxalate treatment resulted in loss of total potash. This was unlike most of the samples. The fact that appreciable K was associated with the amorphous constituents in some of the clay-organic complexes indicated the occurrence of K-zeolites in those samples where the removal of amorphous materials led to a decrease in total K₂O content.

(8) <u>Characterisation of inorganic amorphous constituents extracted from clay-organic complex</u>

The allophane content ranged from 0.014-0.038% in the 14 soil samples studied. Oxalate-extractable iron oxides ranged from 1.345-10.584% in these samples. Though a comparison of the Fe₂O₃ values between soils groups failed to reveal any specific relationship, iron appeared to be the major constituent of the amorphous material. In fact highest content of amorphous iron oxide was found in an Alfisol and the lowest in an Entisol. Alfisols, Ultisols and Entisols had a fairly high content of this constituent in the clay-organic complex. Next in abundance was Al₂O₃, Which was present in relatively higher quantities in Entisols and Alfisols. As such, it was impossible to distinguish this Al₂O₃ either as a free form or as a result of SiO₂ due to the lack of proper technique. However, it played an important role as a binding material in forming the naturally occurring clay-organic complex. The alumina content was generally greater than the silica content in the oxalate-soluble constituents. Although amorphous silica content was low, it was found to occur both as free silicic acid form and as globular allophanes. These conclusions are based on electron-microscopic studies.

(9) <u>X-ray studies</u>

The peroxide-CBD-oxalate treated clay-organic complex was saturated with Mg and K. Following the routine procedure, the cleaned clay samples were analysed using X-ray diffraction. Smectite was the dominant mineral in the three Vertisols. Mica, chlorite, and kaolinite were the other minerals. Siraguppa sample did not have mica; quartz was absent in Indore and siraguppa samples. Mica was the dominant mineral in Bentlu, Mohitnagar, Karnal, Katwa, Jorhat, Henningkonglwa, Palampur and Naddi samples, ranging from 33-84%. The other minerals present were chlorite (absent in Karnal), intergrade minerals (except in Karnal), and kaolinite. Quartz was present in small amounts in some of the samples. Vermiculite was found in small quantities in the Karnal sample. Smectite was the other mineral in small quantities in Katwa and Naddi samples. Interstratified minerals had the dominant share in the Kohima sample, followed by kaolinite, mica, chlorite and quartz. Depending on soil groups, the crystalline minerals were either smectite, mica, or kaolinite. They were dominant in
association with other clay minerals, as is normally expected in this particle size range. The overall properties of these mineral surfaces varied greatly from that of the naturally occurring clay organic complexes of which they form integral parts.

(10) <u>Electron-microscopic studies</u>

The electron microscopic studies of the coarse fractions $(2-0.05 \ \mu)$ as well as finer fractions $(< 0.05 \ \mu)$ revealed that, in general, the aggregate morphology was indistinct when untreated samples were examined. Although different shapes were evident from this study, eg, circular, elongated etc., the crystal morphology appeared only when peroxide treatment was given. Removing free oxides and amorphous materials could only clarify the crystal morphology. It has been observed in several samples where cleaned samples revealed the morphology of mica, kaolinite or smectite crystals. It indicates the association of crystals with organic matter, amorphous materials and other free oxides.

In most cases, untreated samples failed to reveal any definite morphology, and the removal of organic matter could bring the amorphous substances into a clear vision as clear as allophane chains in some cases. Although such allophanes (globular) were found to be free in the naturally occurring clay-organic complex, the peroxide treatment still made their morphology clearer. It leads to the conclusion that the association of organic matter with free oxides and amorphous materials was more common in many of the samples. Such observations find support from the chemical data and the physico-chemical data.

These studies also show that Fe-oxides existed as separate micronodules and were not so much associated with the particles' surface. Besides iron oxides, amorphous materials were also observed to remain individual in these samples; thus, this was more conspicuously visible when organic matter was removed. As mentioned, this indicated that although these materials are coated on the crystalline component of the naturally occurring clay-organic complex, the association was observed more with organic matter, amorphous constituents and iron oxides. These materials have a tremendous surface area, negative charges, and different cation-storage. As a result, their removal, with a few exceptions, has reduced the surface area values, exchange capacity, and content of various cations, as revealed by a chemical and physicochemical analysis of these complexes with different treatments.

The other important observation was the existence of highly siliceous diatomaceious shells in some samples (e.g. Jorhat and Kohima). These were mostly observed in cleaned samples, although still coated with iron oxides. This study's unique feature was the failure to remove the oxide coatings from the mineral surface even after CBD-oxalate treatment. Such was the intimate association of these oxides with crystalline components that several CBD treatments failed to remove the surface crust of these oxides. This was the observation from the work carried out earlier in this laboratory.

The observation made during infrared studies further substantiated the occurrence of organic-amorphous association. Peroxide treatment failed to remove all the organic matter. This resulted in the appearance of C=O bands in peroxide-treated samples. When CBD-oxalate treatment was given,

such bands almost disappeared, suggesting that the removal of amorphous materials also removed part of organic matter.

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BIBLIOGRAPHY

- Adams, W.A. and Stewart, V.I. (1969). The effect of ultrasonic dispersion on Silurian shale particles. Soil Sci. 108 : 227 -8.
- Adhikari, M., Chakraborty, G. and Hazra, G.C. (1972). Fulvic acid metal complexes. J. Indian Soc. Soil Sci. 20(4) 311-21.
- Adhikari, M., Mazumdar, M.K. and Mukhopadhyay, T.K. (1979). Investigation on clay-humus interaction by themo-gravimetric analysis. Fert. Tech. 16(1): 50-53.
- *AkhtyrtseV, B.P., Kader, G.M. and Yarilova, E.A. (1970). Chemico-mineralogical composition of precolloidal and colloidal fractions of Solodized soils of the OK- Don lowland. Pochvovedenie 3 : 92-103.
- Aleksandrova, L.N. (1954). Nature and properties of the products of the interaction of humic acid and humates with sesquioxides. Soviet Soil Sci. 1 : 14-29.
- *Aleksandrova, L N. (1960). The use of sodium pyrophosphate for separating free humic substances and their organo mineral compounds from soil. Pochvoveden ie 2 : 90-92.
- Aleksandrova, L. N. (1967). Organo-mineral humic acid derivatives and methods of studying them. Soviet Soil Sci. 14 : 903-13.
- *Aleksandrova, L.N. and Nad, M. (1958). The nature of organo-mineral colloids and methods for their study. Pochvovedenie 10: 21-27.
- *Aleksandrova, L,N., Zvereva, T.S. and Fomin, Yu, I. (1974) . The formation of organo-mineral colloids. Transactions, 10th International Congress of Soil Science, II : 57-64.
- *Alexiades, C.A, and Jackson, M.L. (1966). Quantitative clay mineralogical analysis of soils and sediments. Proc. 14th Natl. Conf. Clays and Clay Mins. pp. 35-52.
- Allison, F.E. (1973). Soil organic matter and its role in Crop production. Elsevier, Amsterdam, 637 pp.
- Anderson, D.W., Paul, E.A. and St. Arnaud, R.J. (1974). Extraction and characterization of humus with reference to clay associated humus. Can. J. Soil sci. 54(3): 317-323.
- Andrew, R.W., Jackson, M.L. and Wada, K. (1960). Intersalation as a technique for differentiation of kaolinite from chlorite by X-ray diffraction. Soil Sci. Soc. Am. SoC. 24: 422-24.
- *Antipov-Karatayev, I.N., Kellerman, V.V. and Khan, D.V. (1948). Methods of studying soil aggregates. Izd.An. SSSR.
- *Appett, R.H. (1976). Interactions between humic compounds and inorganic ions colloids in soils derived from Volcanic ash. Ciencia e Investigacion Agraria 3(2/3) : 139-146.
- Arai, S. and Kumada, K. (1981). Factors controlling stability of Al-humate. Geoderma 26(1/2): 1-12.
- Arshad, M.A. and Lowe, L.E. (1966). Fractionation and characterization of naturally- occurring organoclay complexes. Soil Sci. Soc. Am. Proc. 30 : 731-35.
- *Atkinson, H,J. and Turner, R.C. (1944). Soil Sci, 57 : 233.

- *Barkoff, E. (1960). The use of ultrasonic waves for increasing reaction speeds and for dispersing the soil in analytical operations. Maataloust, Aikak. 32 : 179-85.
- Barshad, I. (1952). Factors affecting the interlayer expansion of montmorillonite and vermiculite with organic substances. Soil Sci. Soc. Amer. Proc. 16 : 176-182.
- Bear, F.E. (ed.). Chemistry of the Soil. 2nd ed. (1965). Oxford and IBH Pub. Co., New Delhi.
- *Beskrovnyi, A. et al. (1979) . Artificial, biologically active, humus-like substances. Biologicheskie Nanki 3(183) : 85-89.
- Bhattacharyya, T. (1980). Influence of toposequence on the genesis of minerals in the clay fraction of soils derived from granite-gneiss. M.Sc. Thesis, IARI, New Delhi.
- Bodenheimer, W., Heller, L., Kirson, B. et al. (1962) . Organo-metallic clay complexes. Part II. Clay Min. Bull. 5: 145-154.
- Bond, R,D, (1964). The influence of the microflora on the physical properties of soils. II. Field studies on water repellent sands. Aust. J. Soil Res. 2 : 123-31.
- Boudot, J.P. and Bruckert, S. (1978). Organo-metallic complexes and miaroaggregate structures of soils on chloritic minerals of the Vosges Schist greywaeke system. Science du Sol 1: 31-40.
- *Boufils, P. and Dupis, M. (1969). Dispersion of soil colloids with ultrasonic vibration. Bull. Ass. fr, Etude Sol. 1: 13-22.
- Bourget, S.J. (1968). Ultrasonic vibration for particle-size analyses. Can. J. Soil Sci. 48 : 372-73.
- Bradley, W.F. (1954). X-ray diffraction criteria of chloritic material. Clays and Clay Mins. Natn. Acad. Sci. NRC. PUB.No.327, Washington, DC : 324-34.
- *Bremner, J.M. and Lees, H. (1949). Studies on soil organic matter, Part 2, Extraction of organic matter from soil by neutral reagents. J. Agr. Sci. 39(3).
- *Brindley, G.W. (1954). Structural mineralogy of clays. Clays and Clay Technology, California Division of Mines, Bull 169, San Francisco, pp 33-43.
- BroWn, G. (1954). Degrading illite. Nature 173: 644.
- Brown, G. (Ed.) (1961). "X-ray identification and crystal structures of clay minerals" Published by Mineralogical Society, London.
- *Bruckert, S. (1975). A chemical test for differentiation between cambic and spodic horizons. Comptes Rendus Hebdomadares des Seances de l'Academie des Sciences, D 280(11) : 1361-64.
- Bruckert, S. and Kilbertus, G. (1980) . Fractionation and analysis of organo-mineral complexes in brown soils and chernozems. Plant and Soil 57: 271-95.
- *Bruckert, S. and Metche, M. (1972). The dynamics of iron and aluminium in a podzolic environment
 : Characterization of the organo-metallic complexes in spodic horizons. Bull. de l'Ecole
 Superieure d'Agronomie etdes Industries Alimentaries 14(2): 263-75.
- Brydon, J,E, and Sowden, F.J. (1959) . A study of the clay-humus complexes of a chernozemic and a podzol soil. Can. J. Soil Sci. 39 : 136-143 .

- Burdford, J,R., Deshpande, T.L., Greenland, DJ. et al. (1964) . Influence of organic materials on the determination of the specific surface areas of soils. J. Soil Sci. 15 : 192-201.
- *Carballas, M., Cabaneiro, A, Guitan-Ribera, F. And Carballas, T. (1980). Organo-metallic Complexes in Atlantic humiferous soils. Anales de Edafologia Y Agrobiologia 39(5/6) : 1033-43.
- Carter, D.L., Heilman, M.D. and Gonzalez, C.L. (1965). Ethylene glycol, monoethyl ether for determining surface area of silicaténinerals. Soil Sci. 100: 356-60.
- *Cegarra, J., Metche, M. and Jacquin, F. (1978) . The study of the organo-cationic phosphorus complexes in soils . Comptes Rendus Hebdomadaries des Seances de l'Academie des Sciences, D.287 (5): 451-54.
- *Cita, C. (1964). VIIIth Int. Congr. of Soil Sci, Abstractof papers VII, Bucharest.
- *Chassin, P. (1976). Influence of organic matter on clay properties. Results of model studies. Science du Sol. 2 : 115-20.
- Chassin, P., Berre, B. Le and Nakaya, N. (1978). Influence of humic substances on clay properties. IV Hydration of montmorillonite-humic acid associations. Clay Minerals 13(1): 1-16.
- *Chassin, P., Berre, B. Leand Nakaya, N. (1977). The effect of humic substances on the properties of clays. The importance of the method of preparation on the hydration properties of the montmorillonite humic acid complexes. Comptes Rendus Hebdomadaires des Seances de 1' Academie des Sciences, D.284(17) :1659-62. Chakravarti, S.K. (1956). Sedimentation volume and zeta potential of pure clay minerals and their mixtures as influenced by quaternary ammonium compounds. Sci. And Cult. 22 : 170-72.
- Chatterjee, Monika and Ghosh, Kunal (1981). Influence of hydrothemal conditions of the nature and properties of humic substances. J. Indian Soc. Soil Sci, 29: 184-89.
- Chaudhury, M.B. and Stevenson, F. (1957). Chemical and physico-chemical properties of soil humic colloids. III. Extraction of organic matter from soils. Soil Sci. Soc. Am. Proc. 21: 508-13.
- Chen, Y. and Schnitzer, M. (1976). Scanning electron microscopy of a humic acid and of a fulvic acid and its metal and clay complexes. Soil Sci, Soc. Am. Proc. 40(5): 682-86.
- *Clare, K.E. (1947). The influence of cultivation on soil structure and its assessment in soils of variable mechanical Composition. J. Coun. Sci. Industr. Res. Aust. 20: 162-75.
- *Crowley, M.S. and Welch, P.A. (1954). J. Amer. Ceram, Soc. 37(9).
- *Crawford, A.E, (1955). Ultrasonic engineering. Butterworths Scientific Publications, London.
- *Deshpande, T.L., Greenland, D.J. and Quirk, J.P. (1964). Charges on iron and aluminium oxides in soils. Trans. 8th int. Congr. Soil Science., Bucharest 3: 1213-25.
- Deshpande, T.L., Greenland, D.J. and Quirk, J.P. (1968). Changes in soil properties associated with the removal of iron and aluminium oxides. J. Soil Sci. 19 : 108-22.
- De Villiers, J.M. (1971). The problem of quantitative detemination of allophane in soil. Soil Sci. 112 : 2-7.

- *Dickson, D.P.E., Heller-Kallai, L. and Rozenson, I. (1979). Mossbauer spectroscopic studies of iron in organic material from natural sedimentary environments. Geochemica et Cosmochimica Acta 43(9): 1449-53.
- Dixon, J.B. and Jackson, M,L. (1959) . Dissolution of interlayers from intergradient soil clays after preheating at 400°C. Science 129: 1616-17.
- Dormaar, J.F. (1974). Scanning electron microscopy as applied to organo-mineral complexes in alkaline extracts of soil. Soil Sci. Soc. Am. Proc. 38(4): 685-86.
- Dubach, P. and Mehta, N.C. (1963). The chemistry of soil humic substances. Soils and Ferts. 26: 293-300.
- *Duchaufour, P. (1963). A note on the role of iron in organo-mineral conplexes. C.R. Acad. Sci. Paris 256: 2657-60.
- Duchaufour, P. (1976) Dynamics of organic matter in soils of temperate regions : Its reaction on pedogenesis. Geoderma 15(1): 31-40.
- Dudas, M.J. and Pawluk, S. (1968). Chernozen soils of the Alberta Parklands. Geoderma 3(1): 19-36.
- Dudas, M.J. and Pawluk, S. (1969/1970). Naturally occurring organo-clay complexes of orthic black chernozens. Geoderma 3 : 5-17.
- *Dupis, T. and Jambu, P. (1973). Some properties of calcium humates and calcium fulvates. Competes Rendus Hebdomadaires des Seances de l'Academic des Sciences, D.276(4) : 489-92.
- *Dupis, T., Jambu, P. and Righi, D. (1979). Reaction of fulvic acids with metallic hydroxides. Aluninium hydroxides. Pedologie. 29(2): 191 -207.
- Edwards, A.P. and Bremner, J. M. (1964). Use of sonic vibration for separation of soil particles. Can. J. Soil sci. 44: 366.
- Edwards, A.P. and Bremner, J.M. (1967a). Dispersion of soil particles by sonic vibration. J. Soil Sci. 18: 47-63.
- Edwards, AP. and Brenner, J.M. (1967b). Microaggregates in soils. J. Soil sci. 18: 64-73.
- *El'piner, I. Ye (1963). Ultrasonics, physico-chemical and biological action. Fizmatigiz, Moscow.
- *El'Piner, I.E. (1964). Ultrasound: Physical, chemical and biological effects. Consultants Bureau, N.Y.
- Emerson, W.W. (1959). The structure of Soil crumbs. J. Soil Sci. 10: 235-44.
- *Eschena, T. (1963) . Some physico-chemical properties of clay-humus complexes. Agrochimica 7: 369-73.
- Farmer, V.C. and Mitchel, B.D.(1963). Occurrence of oxalates in soil clays following hydrogen peroxide treatment. Soil Sci. 96 : 221-29.
- *Farmer, V.C., Russell, J.D., McHardy, W.J., Newman, A.C.D., Ahbrichs, J.L. and Rimsaite, JYH. (1971). Evidence for loss of protons and octahedral iron fromoxidised biotites and vermiculites. Min, Mag. 38: 121-37.
- *Felbeck, G.T. Jr. (1959). The chemistry of Soil organic matter: I. Effect of ultrasonic irradiation on the extraction of organic matter from soil with inorganic reagents. Agron. Abstr. p. 17.

- Fey, M.V. and Roux Le, J. (1975). Quantitative determination of allophane in soil clays. In Proc. Int. Clay Conf.1975, Mexico City (Edited by Bailey, S.W.), pp. 451-64 : Applied Publ., Wilmette, II.
- *Fickendy, E. (1906). J. Landw. 54:343.
- *Flip, Z. (1968). A contribution to a spectrophotometric study of the humus-clay complex. Rostl. Vyroba 14 (XLI): 697-706.
- Follett, E.A.C. (1965). The retention of amorphous, colloidal ferric hydroxides by kaolinites. J,Soil Sci. 16: 334-41.
- Follett, E.A,C., McHardy, W.J., Mitchell, B.D. and Smith, B.F.L. (1965) . Chemical dissolution techniques in the study of soil clays: Part I. Clay Minerals 6: 23-34.
- Fordham, A. W. and Norrish, K. (1979). Electron microprobe and Electron microscope studies of soil clay particles. Aust. J. Soil Res. 17(2) : 283-306.
- *Fripiat, J.J. and Gastuche, M.C. (1952). Etude physic-chemique des surfaces des argiles. Inst. Nat. Et. Agron. Congo Belge Pub Ser Sci. 54.
- *Fu, C.P. and Chang, C .S. (1978). Effect of green manure on the properties of colloidal complexes of clayey warp soil. Acta Pedologica Sinica 15(1): 83-94.
- *Ganev, S. (1972). The mechanism of bonding between humic fractions of the absorption complex in podzolized soils. "p"rvi Natsionalen Kongres po Pochvoznanie, Bulgaria 1969 : 269-76.
- Garrett, W.G. and Walker, G.F. (1962). Swelling of some vemiculite-organic complexes in water. Clays and Clay Min. 9: 557-67.
- *Gata, G.H. (1964). The effect of ultrasonic fields on suspensions of clay minerals. Trans. 8th Int. Congr. Soil Sci., Bucharest 3 : 1165-74.
- Gessa, C., Melis, P., Bellu, G. and Testini, C. (1978). Inactivation of clay pH-dependent charge in organo-mineral complexes. J. Soil Sci. 29(1): 58-64.
- Gessa, C., Melis, P., Solinas, V. and Testini, C. (1978a). Effect of organic matter on phosphate sorption by organo-mineral complexes. Agrochimica 22(5-6) : 507-17.
- Ghabru, S.K. (1977). Chemical and mineralogical studies on some typical soil profiles of Himachal Pradesh. M.Sc. Thesis, IARI, New Delhi.
- Ghosh, K. and Schnitzer, M. (1981). Flourescence excitation spectra and viscosity behavior of a fulvic acid and its copper and iron complexes. Soil Sci. Soc. Am. J. 45(1): 25-29.
- Ghosh, S.K. and Datta, N.P. (1972). X-ray investigation of clay minerals in the soils of WestBengal. Proc. Indian natn. Sci. Acad. B.40: 138-50.
- Ghosh, S.K., Das, S.C. and Mehta, S.C. (1962). Mineralogy of clays of red and lateritic soils. J. Scient. ind. Res. 21D : 339-41.
- *Giovannini, G. and Sequi, P. (1978). Interaction between soil organic matter and polyvalent metals (Abstract). In Modification of soil structure (Emerson, W.W., Bond, R.D. and Dexter, A.R.-Editors). Chichester, U.K. John and Wiley and Sons : 199- 201.

- Gjems, O. (1967). Studies on clay minerals and clay mineral formation in soil profiles in Scandinavia. Meddelelser fro Det Norske Skogforsoksvesen, No.81 Bind 21, Vollbeekk, Norway.
- *Godlin, M.M. (1959). Physical clays of soils and their coefficient of humus saturation. Dopov. Ukr, Akad. Sil'skogospodars'K Nauk. 2 (4): 26--29.
- Goodman, B.A. and Cheshire, M.V. (1979) . A Mossbauer spectro-scopy study of the effect of pH on the reaction between iron and humic acid on aqueous media. J. Soil Sci. 30(1): 85-91.
- *Gonzalez Carcedo, S. and Fuente Marcos, M.À. (1980). Organo-metallic complexes in microaggregates from an umbric dystrochrept. Anales de Edafologia Y Agrobiologia 39(5/6) : 845-57.
- Gorbunov, N.I. and Orlov, D.S. (1977). Nature and strength of the bond of organic substances with soil minerals. Soviet Soil Science 9(4) : 465-76.
- Greenland, D.J. (1965a). Interaction between clays and organic compounds in soils. Part 1. Mechanisms of interaction between clays and defined organic compounds. Soils and Ferts. 28(5): 415-25.
- Greenland, D,J. (1965b). Interaction between clays and organic compounds in soils. Part II. Adsorption of soil organic compounds and its effect on soil properties. Soils and Ferts. 28(6): 521-32.
- Greenland, D.J. (1971). Interactions between humic and fulvic acids and clays. Soil Sci. 111: 34-41.
- Greenland, D.J. (1975). Charge characteristics of some kaolinite-iron hydroxide complexes. Clay Min. 10: 407-16.
- *Greenland, D.J. and Quirk, J.P. (1962). Surface areas of soil colloids . Proc. int. Soc. Soil Sci. Comm. 4-5, New Zealand, pp. 79-87.
- *Greenland, D.J. and Oades, J.M. (1968). Iron hydroxides and clay surfaces. Trans. 9th Int. Cong. Soil Sci., Adelaide, 1: 657-668.
- *Greenland, D.J. and Wilkinson, G.K. (1969). Use of electron microscopy of carbon replicas and selective dissolution analysis in the study of the surface morphology of clay particles from soils. Proc. Int. Clay. Conf., Tokyo 1 : 861-70.
- Greenland, D.J. and Hayes, M.H.B. (1978) (Ed.) "The Chemistry of Soil Constituents", John Wiley and Sons.
- *Greenland, D.J., Laby, R.H. and Quirk, J.P. (1962). Adsorption of glycine and its di- tri-, and tetrapeptides by montmorillonite. Trans. Faraday Soc. 58 : 829-41.
- Greenland, D.J., Quirk, J.P. and Theng, B.K.G. (1964). Influence of increasing proportions of alkylammonium ions on the swelling of calcium montmorillonite in Water. J. Colloid Sci. 19: 837-40.
- *Greenland, D.J., Laby, R.H. and Quirk, J.P. (1965). Adsorption of amino acids and peptides by montmorillonite and illite. Part II. Physical adsorption. Trans. Fafaday Soc.
- Greenland, D.J., Oades, J.M. and Sherwin, T.W. (1968). Electron microscope observations of iron oxides in some red soils. J. Soil Sci. 19: 116-22.

- Griffith, S.M. and Schnitzer, M. (1975). The isolation and characterization of stable metal-organic complexes from tropical volcanic soils. Soil Sci. 120(2): 126-31.
- *Griffith, S.M. and Schnitzer, M. (1976). Isolation and characterization of metal-organic complexes from tropical volcanic soils. In Environmental Biogeo-chemistry. Vol.1, Carbon, Nitrogen, Phosphorus, Sulfur and Selenium Cycles. Proc. 2nd Int. Symp. on Environ. Biogeochemistry, Hamilton, Ontario, Canada, April 8-12th, 1975 (Nriagu, J.D. Editor) Ann Arbor, USA, Ann Arbor Science : 117-30.
- Grim, R.E. (1968). Clay Mineralogy, 2nd Edn., McGraw-Hill Book Co.
- Grim, R.E. and Johns, W.D. (1954). Clay mineral investigation in northern Gulf of Mexico. Clays and Clay Mins. Natn. Acad. Sci., NRC Pub. No.327, Washington, DC:81-103.
- Gupta, R.D., Tripathi, B.R. and Banerjee, S.K. (1982) Composition and nature of humus in some soils of north-west Himalayas as influenced by vegetation, climate and parent rock. J. Indian Soc. Soil Sci. 30: 468-76.
- Habibullah, A.K.M, and Greenland, D.J. (1971). Clay mineralogy of some seasonally flooded soils of East Pakistan. J. Soil Sci. 22: 179-90.
- Hamblin, A.P. and Greenland, D.J. (1977). Effect of organic constituents and complexed metal ions on aggregate stability of some East Anglian soils. J. Soil Sci. 28(3) 410-16.
- Hashimoto, H. and Harada, T. (1959). Studies on the organo-mineral colloidal complexes of paddy soil.IV. Humus accumulated on GI colloidal complexes of high-yielding paddy soil. Soil and Plant Food 5: 49-53.
- Hashimoto, I. and Jackson, M.L. (1960). Rapid dissolution of allophane and kaolinite-halloysite after dehydration. Clays and clay Minerals. Proc. 7th Conf.: 102-13.
- Hendricks, S.B. (1941). Base-exchange of the clay mineral montmorillonite for organic cations and its dependence upon adsorption due to van der Waals force. J. Phys. Chem. 45: 65-81.
- *Hetier, J.M., Jerez, F.G. and Bruckert, S. (1974). Electron microscopy and the composition of organomineral complexes in andosols. Comptes Rendus Hebdomadaires des Scances de 1'Academie des Sciences, D. 278(22) : 2735-37.
- Hinds, A.A. and Lowe, L.E. (1980). Dispersion and dissolution effects during ultrasonic dispersion of gleysolic soils in water and in electrolytes. Can. J. Soil Sci. 60:329-35.
- *Houbenov, G., Behar, A. and Khalil, P. (1979). Changes in the interlamellar spaces of montmorillonite during interactions with humic and fulvic acids. Pochvonzananie Agrokhimiya 14(2) : 91-97.
- *Hughes, D.E. (1961). The disintegration of bacteria and other microorganisms by the M.S.E.- Mullard ultrasonic disintegrator. J. Biochem. Microbiol. Technol. Eng. 3: 405-33.
- *Inoue, T.A. (1973). A preliminary study of organo-mineral complexes in a glassy volcanic ash soil containing imogolite and allophane as principal clay minerals. Pedologist 17(1) : 26-36.
- Jacks, G.V. (1963). The biological nature of soil productivity. Soils and Ferts. 26: 147-50.

- Jackson, M.L. (1956). "Soil Chemical Analysis-Advanced Course" Published by the author, Dept. of Soil Sci., Univ. of Wisconsin, Madison.
- Jackson, M.L. (1963a). Aluminium bonding in soils : A unifying principle in soil science. Soil Sci. Soc. Am. Proc. 27 :1-10.
- Jackson, M.L. (1963b). Interlayering of expansible layer silicates in soils by chemical weathering. Clays and Clay Minerals. 11th Conf., Pergamon Press, London 29-46.
- Jackson, M.L. (1973). "Soil Chemical Analysis", Prentice Hall of India, Pvt. Ltd., New Delhi. pp 498.
- Jackson, M.L., Whittig, L.D., Vanden, Heuvel, R.C., Kaufman, A. and Brown, B.E. (1954). Some analysis of soil montmorin, vermiculite, mica, chlorite and interstratified layer silicates. Clays and Clay Mins. Natn. Acad. Sci. NRC Pub. No.327, Washington, DC : 218-40.
- Jambu, P., Dupui S. T. and Dupuis, J. (1972). A study of some aspects of iron fixation by humic acids. Annales Agronomiques 23(3) : 333-54.
- *Kampf, N. (1981). Die Eisenoxidmineralogie einer Klimasequenz Van Boden aus Eruptiva in Rio Grande do Sul, Brasilien. Dissertation.
- Karickhoff, S.W. and Bailey, G.W. (1976). Protonation of organic bases in clay-water systems. Clays and Clay Min. 24(4) : 170-76.
- Kaurichev, I.S., Karpukhin, A.I. and Stepanova, L.P. (1979). Study of the composition and stability of water-soluble organo iron complexes. Soviet Soil Sci. 11 : 120.
- *Khan, D.V. (1951). Methods of studying the composition of water-soluble organic substances of plant residues. Trudy Pochr. Inst. Dukuchaeva 38 : 99-107.
- Khandekar, À,V. (1980). Mineralogy and potassium chemistry of some black soils. Ph.D. Thesis, IARI, New Delhi.
- Kitagawa, Y. (1983). Goethite and hematite in some soils from the Amazon region. Soil Sci. Pl. Nutr. 29(2) : 209-17.
- *Kodama, H. and Schnitzer, M. (1969). Thermal analysis of a fulvic acid-montmorillonite complex. Proc. 3rd int. clay Conf. 1969. 1 : 769-74.
- Kodama, H. and Schnitzer, M. (1977). Effect of fulvic acid on the crystallization of Fe(III) oxides. Geoderma 19(4) : 279-91.
- Koms'ka M.S., Dolin, I. and Fes'ko, Zh. Z. (1966). Ultrasonic selective dispersion of admixtures in kaolin . Legk. Prom. 1966 (4) : 23-25.
- *Kononova, M.M. (1963). Soil organic matter. Izd. An SSSR.
- Kononova, M.M. (1966). Soil organic matter. Its nature, its role in soil fomation and in soil fertility, 2nd Edition, Pergamon Press, Oxford.
- *Kononova, M.M. and Bel'Chikova, N,P. (1972). Methods for extracting and studying iron and aluminium containing humus complexes from soil. In P"rvi Natsionalen Kongress po Pochvoznanie, Bulgaria, 1969. Sofia, Bulgaria, Bulgarian Academy of Sciences : 277-86.

- *Kononova, M.M., Alexandrova, I.V. and Titova, N.A. (1964). Decomposition of silicates by soil organic matter. Pochvovedenie, No. 10 : 1-12.
- *Kribek, B-, Kaigl, J. and Oruzinsky, V. (1977). Characteristics of di and trivalent metal humic acid complexes on the basis of their molecular weight distribution. Chemical Geology 19(1): 73-81.
- Krishna Murti, G.S.R., Moharir, A.V. and Sarma, V.A.K. (1970). Spectrophotometric determination of iron with ortho-phenantrhroline. Microchem. J. 15 :585-89.
- *Kruglitskii, N.N., Orcharenko, F.D., Simurov, V.V. et al.(1966). Mechanism of formation of coagulation structures in aqueous dispersions of palygorskite and hydromica under ultrasonic effect. Izv. Akad. Nauk, SSSR - neorg. Mater. 2: 2213-20.
- *Krystanov, S., Stivenson, F. and Aradakani, M.S. (1972). Complex-forming properties of humic acid. Pochvoznanie Agrokhimiya 7(5) : 29-34.
- *Kukharenko, T.A. (1946). Humic acid reactions with heavy metallic salts. Zh. prikl. Khim, No.2.
- *Kumada, K. and Aizawa, K. (1959). The infrared absorption spectra of soil components. Soil Plant Food 4 : 181-88.
- *Kuron, H., Preusse, H.U. and Fohrenbacher, A. (1961).Colloid-chemical and clay-mineralogical examinations of two profiles from Wasermach, Z. PflErnahr. Dung. 92 : 233-47.
- *Kusano, S. (1936). The effect of ultrasonic waves on potassium iodide and hydrogen peroxide. Tohoku J. exp. Med. 30: 175-80.
- *Kuznicki, F. and Sklodowski, P. (1969). Effect of soil forming processes on iron and aluminium Contents of organic-mineral complexes. Roczniki g' ebozn. 20 : 3-23.
- Lai, O.S. and Swindale, L.D, (1969). Chemical properties of allophane from Hawaiian and Japanese soils. Soil Sci. Soc. Am. Proc. 33 : 804-08.
- Larson, G.O. and Sherman, L.R. (1964). Infrared spectro-photometric analysis of some carbonyl compounds adsorbed on bentonite clay. Soil Sci. 98 : 328-31.
- *Legally, G., Weiss, A., Perez Rodriguez, J.L, and Gonzalez, Garcia, F. (1976). A natural clay-organic complex from black Andalusian earth. In Proc. Int. Clay Conf. Mexico city, July 16-23, 1975 (Bailey, S.W. Ed.), Wilmette, Illinois, USA, Applied Pub. Ltd, 659-60.
- Linahan, D.J. (1978). Humic acid and iron uptake by plants. Plant and Soil 50(3): 663-70.
- Lutwick, L.E. (1972). Thermal decomposition reactions of Clay-organic matter complexes and organic matter separated from a black chernozemic soil. Can. J. Soil Sci. 52(3): 417-25.
- MacEwan, D.M.C. (1944). Identification of the montmorillonite group of minerals by X- rays. Nature 154: 577-78.
- *MacEwan, D.M.C. (1946). Identification of montmorillonite. J. jSoc. Chem. Ind. 65: 98-305.
- *MacEwan, D.M.C., Amil, R.A. and Brown, G. (1961). Interstratified clay minerals. The X-ray identification and crystal structures of clay minerals. ed. G. Brown, Mineralogical society, London 393-445.

- *MacKenzie, R.C. and Meldau, R. (1959). The ageing of sesquioxide gels : 1. Mineralog. Mag. 32: 153-65.
- *Manskaya, S.M., Drozdova, T.V. and Yemel'yanova, M.P. (1958). Binding of copper by various forms of natural organic compounds. Pochvovedeniye No.6.
- *Manskayaya, S.M. and Drozdova, T.V. (1964). Geochemistry of Organic matter. Izd. "Nauka".
- Marok, A.S. (1980). A study on the nature of aluminium uronide complexes in soil. Indian J. Agril. Res. 14(3): 143-46.
- *Martin Martinez, F. and Perez Rodriquez, J.L. (1969). Interlamellar adsorption of black earth humic acid on Na-montmorlllonite. Z. P flErnahr. Bodenk. 124: 52-57.
- *Matthiat, B. (1964). Beitr. Mineral. Petrogr. No.2, Berlin.
- *Mathieu-Sicaud, A. and Levavasseur, G. (1948). Compt, rend. 227, Paris.
- *Mathieu-Sicaud, A. and Levavasseur, G. (1949). Ultrasonic dispersion of clay suspensionsinterpretation of the results with an electron microscope. C.R. Acad. Sci. Paris 228: 393-95.
- Mattson, S. (1930). The laws of soil colloidal behaviour. III. Isoelectric precipitates. Soil Sci. 30: 459-95.
- Mattson, S. (1932). The law of soil colloidal behaviour. IX. Amphoteric reactions and isoelectric weathering. Soil Sci. 34: 209-239.
- McHardy, W.J., Thompson, A.P., Goodman, B.A. (1974). Formation of iron oxides by decomposition of iron phenolic chelates. J. Soil Sci. 25(4): 471-82.
- *Medvedeva, A.M. and Sergeyev, L.A. (1962). Disintegration of rocks and separation of spores and pollen using ultrasonics. In : Physical methods of studying sedimentary rocks and minerals. Izd. Akad. nauk SSSR.
- Mehra, O.P. and Jackson, M.L. (1960). Iron oxide removal from soils and clays by a dithionite citrate system buffered with sodium bicarbonate. Clays and Clay Mins. 7th Conf. Pergamon Press, London: 317-27.
- *Miesel, T., Lakatos, B. and Mady, G. (1977). Biopolymer-metal complex systems. VII. Ion exchange and redox capacity of peat humic substances. Agrokemia es Talajtan 26(3/4) : 269-80.
- Mitchell, B.D. Farmer, V.C. (1962). Amorphous clay minerals in some Scottish soil profiles. Clay Minerals Bull. 5: 128-44.
- Mitchell, B.D., Farmer, V.C. and McHardy, W.J. (1964). Amorphous inorganic material in soils. Adv. Agron. 16: 327-83.
- Mortland, M.M. (1970). Clay-organic complexes and interactions. Adv. Agron. 22:75 117.
- Mukerjee, N, (1956). Studies of the nature of humus and clay-humus Complex. J. Indian Chem. Soc. 33: 744-48.
- Mukhopadhyay, N., Gupta, S.K. and Banerjee, S.K. (1982). Forms and distribution of humic and fulvic acid components in soils under deciduous and coniferous forests. Indian Soc. Soil Sci. 30(4) : 477-83.

- Murray. H.H. and Sayyeb, A.S. (1955). Clay mineral studies of some recent sediments of the North Carolina Coast. Clays and Clay Mins. Natn. Acad. Sci. NRC Pub. No. 395, Washington, DC: 430-41.
- *Myers, H.E. (1937). Soil Sci. 44: 331.
- *Najmr, S. (1963). Results of investigation on the humus-clay complex of soils in Czechoslovakia. Ust. Ved. Inf . MZLVH 36 : 241-52.
- Oades, J.M. (1964). The nature and distribution of iron compounds in soils. Soils and Fert. 26: 69-80.
- *Olmstead, L.B. (1931). Dispersion of soils by a supersonic method. J. agric. Res. 42: 841-52.
- Perez Rodriguez, J.L., Weiss, A. and Legaly, G. (1977). A natural clay-organic complex from Andalusian black earth. Clays and Clay Min. 25(3): 243-51.
- Perrott, K.W. (1978a). The influence of organic matter extracted from humified clover on the properties of amorphous aluminosilicates. I. Surface charge. Aust. J. Soil Res. 16(3): 327-39.
- Perrott, K.W. (1978b). The influence of organic matter extracted from humified clover on the properties of amorpohous aluminosilicates. II. Phosphate retention. Aust. J. Soil Res. 16(3): 341-46.
- *Puri, A.N. and Keen, B.A. (1925). The dispersion of soil in water under various conditions. J. agric. Sci., Camb. 15 : 147-61.
- Quirk, J.P. and Panabokke, C.R. (1962). Incipient failure of soil aggregates. J. Soil Sci. 13: 60-70.
- *Ramamoorthy B., Singh, M.M. and Guha, M.M, (1957). The formation of clay-humus complexes and their significance in some Indian soils. Carr. Sci. 26 :84-85.
- Raman, K.V, and Mortland, M.M. (1969/70). Amorphous materials in a Spodosol : Some mineralogical and chemical properties. Geoderma 3 : 37-43.
- Ram Nand and Raman, K.V, (1981). Characterization of humic and fulvic acids extracted from different Indian soils. J. Indian Soc. soil Sci. 29 : 179-83.
- Rashid, M.A., Buckley, D.E. and Robertson, K.R. (1972). Interaction of a marine humic acid with clay minerals and a natural sediment. Geoderma 8 : 11-27.
- *Raychaudhuri, S.P. (1964). Land Resources of India, Vol. I, Committee on natural resources, Planning Commission, Govt. of India.
- Rich, C.I. (1960). Aluminium in interlayers of vermiculite. Soil Sci. Soc. Am. Proc. 24 : 26-32.
- Rich, C.I. (1967). Hydroxy interlayer in expansible layer silicates. Clays and Clay Mins. 16: 15-30.
- Rich, C.I. and Kunje, G.W. (1964). Soil clay mineralogy À Symposium. The Univ. of North Carolina Press, Chapel Hill.
- Rich, C.I. and Obenshain, S.S. (1955). Chemical and clay mineral profile of a red yellow podzolic soil derived from muscovite-schist, Soil Sci. Soc. Am. Proc. 19: 334-39.
- Roberson, H.E., Weir, A.H. and Woods, R,D. (1968). Morphology of particles in size-fractionated Namontmorillonites. Clays Clay Miner. 16 : 239-47.

- *Rolfe, B.N. (1954). Mineralogy of soil profiles: Iredell and Durham soils from the Piedmont Province of North Carolina. Clays and Clay Mins., Natn. Acad, Sci. NRC Pub. No. 327, Washington, DC : 183-89.
- *Roth, C.B., Jackson, M.L., de Villiers, J.M. and Volk, V.V. (1967). Surface colloids on micaceous vermiculite. Trans. Comm. II and IV, Int. Soc. Soil Sci. Aberdeen 217-21.
- Roth, C.B., Jackson, M.L. and Syers, J.K. (1969). Deferration effect on structural ferrous-ferric iron ratio and c.e.c. of vermiculites and soils. Clays Clay Min. 17: 253-64.
- Russell, E.W. (1973). "Soil conditions and plant growth". 10th Edition, E.L.B.S. and Longman.
- Sachdev, M.S. and Deb, D.L. (1982). Effect of application of organo-mineral fertilizers on humic acid characteristics in alluvial soil. J. Indian Soc. Soil Sci. 30 258-63.
- Saly, R. (1967). Use of ultrasonic vibration for dispersing soil samples. Soviet Soil Sci. 11: 1547-59.
- Satoh, T. (1976). Isolation and characterization of naturally occurring organo-mineral complexes in some volcanic ash soils. Soil Sci. Plant Nutr. 22(2) : 125-36.
- Satoh, T. and Yamane, I. (1971). On the interlamellar complex between montmorillonite and organic substance in certain soil. Soil Sci. Plant Nutr. 17: 181-85.
- Satoh, T. and Yamane, I, (1972a). Separation of naturally occurring organo-mineral complexes and their characteristics. 1. Separation by particle size fractionation. J. Science Soil and Manure, Japan 43(1): 41-45. Cited From Soil Sci. Pl. Nutr. 20: 95.
- Satoh, T. and Yama ne, I. (1972b). Separation of naturally occurring organo-mineral complexes and their characteristics. 2. Separation by densimetric fractionation. J. Science of Soil and Manure, Japan. 43(2): 61-65. Cited From Soil Sci. Pl. Nutr. 20: 96.
- Sawhney, B.L. and Jackson, M.L. (1958) . Soil montmorillonite formulas. Soil Sci. Soc. Am. Proc. 22: 115-18.
- Sawhney, B.L. (1960). Weathering and aluminium interlayers in a soil catena. Hollis-Charlton-Sutton-Leicester. Soil Sci. Soc. Am. Proc. 24 : 221-26.
- Scharpenseel, H.W. (1966). Formation and type of bonding of clay-humi acid complexes. I. Formation during shaking experiments and precipitation radiometry. II, Hydro-thermal synthesis of clayhumic acid and other organo- mineral complexes; X-ray, infra-red spectrometer and electron microscopic investigation. Z. P flErnahr. Dung. Bodenk. 114 : 175-203.
- *Scharpenseel, H.W. (1968). Formation and type of bonding of clay-humic acid complexes. III. Further results from precipitation-radiometry and hydrothermal syntheses. Z. Pfl Ernahr. Bodenk. 119: 208-16.
- *Scharpenseel, H.W. and Krause, E. (1972). Amino acids in clay-humic acid complex formation. In "Isotopes and radiation in soil plant relationships including forestry". Proc. Symp. Vienna, 13-17 December 1971. Vienna, Austria, International Atomic Energy Agency (1972): 193-210.

*Schloesing, C.R. (1874). Comp. Reud, 1874, 78 : 1276.

- *Schnitzer, M. (1968). Reactions between organic matter and inorganic soil constituents. Trans. 9th Int. Congr. Soil Sci., Adelaide, 1 :635-42.
- Schnitzer, M. (1969). Reactions between fulvic acid, a soil humic compound and inorganic soil constituents. Soil Sci. Soc. Am. Proc. 33 : 75-81.
- Schnitzer, M, (1977). In : Proc. Int. Symp. Soil Organic Matter, 3rd, Braunschweig, IAEA, Vienna pp. 117-32.
- Schnitzer, M. (1978). In Soil Organic Matter (M. Schnitzer and S.U. Khan, Ed.), Elsevier, Amsterdam.
- Schnitzer, M. and Kodama, H. (1967). Reactions between podzol fulvic acid and Na- montmorillonite. Soil Sci. Soc. Am. Proc. 31 : 632-36.
- Schnitzer, M. and Khan, S.U. (1972). Humic substances in the environment. Marcel Dekker, New York, N.Y. 327 pp.
- Schnitzer, M. and Skinner, S.I.M. (1963a). Organo-metallic interactions in soils. I. Reaction between a number of metal ions and the organic matter of a podzol Bh horizon. Soil Sci. 96 : 86-93.
- Schnitzer, M. and Skinner, S.I.M. (1963b). Organo-metallic interactions in soils. 2. Reactions between different forms of iron and aluminium and the organic matter of a podzol Bh horizon. Soil Sci. 96 : 181-86.
- Schnitzer, M. and Skinner, S.I.M. (1964). Organo-metallic interactions in soils. 3. Properties of ironand aluminium- organic matter complexes, prepared in laboratory and extracted from a soil. Soil Sci. 98 : 197-203.
- *Schwertmann, U. (1965). Formation of goethite and haematite from amorphous ferric hydroxide. Z. Pfl. Ernahr. Dung. Bodenk. 108 : 37-45.
- Schwertmann, U. (1966). Inhibitory effect of soil organic matter on the Crystallization of amorphous ferric hydroxide. Nature, London 212 : 645-46.
- Schwertmanns U. and Fischer, W.R. (1966) . Formation of α Fe O.OH and γ -Fe₂O₃ from amorphous ferric hydroxide. 2.anorg. allg. Chem. 346 : 137-42 .
- Schwertmann, U. and Taylor, R.M. (1982). The significance of oxides for the surface properties of soils and the usefulness of synthetic oxides as models for their study. Bulletin ISSS No.60 : 62-66.
- *Schwertmann, U., Fischer, W.R. and Papendorf, H. (1968). The influence of organic compounds on the formation of iron oxides. Trans. 9th Int, Congr. Soil Sci., Adelaide, 1 : 645-54.
- *Sedletsky, I.D. and Tatarinova, L. (1941). Pedology 9: 33.
- Sehgal , J.L. and, Cornick, F.De (1971). Identification of 14 and 7 A clay minerals in Puniab soils. J. Indian Soc. Soil Sci. 19 : 159-66.
- *Sideri, D.I. (1936). Soil Sci. 42 : 461.
- Shutov, V.D., Kats, M. Ya and Baranov, V.V. (1961) . Use of ultrasonis in the mineralogic analysis of sedimentary rocks. Izv. Akad. nauk SSSR, Ser. geol. 4.
- Shutov, V.D., Kats, M.Y. and Baranov, V.V. (1962) . Use of ultrasonics in mineralogic studies. In Physical methods of studying sedimentary rocks and minerals. Izd. Akad. nauk SSSR.

- Singh, S. (1956). The formation of dark coloured clay- organic complexes in black soils. J. Soil Sci. 7: 43–48.
- *Sipos, S., Sipos, E., Dekany, I., Deer, A., Meisel, J. and Lakatos, B. (1978). Biopolymer-metal complex systems. 2. Physical properties of humic substan ces and their metal complexes. Acta Aqronomica Academiae Scientiarum Hungaricae 27 : 1-2.
- *Sollner, K. (1938). Notes on the dispersion of solids in liquids by ultrasonic waves. Trans. Faraday Soc. 34 : 1170-74.
- *Springer, U. (1936). Zur Kenntnis der Bindungsformen der Humusstoffe, besonders in Waldboden. Z. Pflanzenernahr, Dung., Bodenk. Vol. 45.
- *Stepanov, I.S. (1970). Infrared spectra of finely dispersed fractions of soils. Dokl. Akad. Nauk. SSSR. 193 : 199-202.
- *Stephen, I. and MacEwan, D.M.C. (1949) . Bull. clay Min. 1:157.
- Stevenson, F.J. (1977). Nature of divalent transition metal complexes of humic acids as revealed by a modified potentiometric titration method. Soil sci. 123(1) : 10-17.
- Stevenson, F.J., Marks, J.D., Varner, J.E. and Martin, W.P. (1952). Electrophoretic and chromatographic investigations of clay-adsorbed organic colloids. I. Preliminary investigations. Soil Sci. Soc. Am. Soc. 16 : 60-73.
- *Tan, K.H. and McGreery, R.A. (1976). Humic acid complex fomation and intemicellar adsorption by bentonite. In Proc. Int. Clay Conf., Mexico City, July 16-23, 1975 (Bailey, S.W., Editor), Wilmette, Illinois, USA, Applied Pub. Ltd. 629-41.
- Tamura, T. (1956). Physical, chemical and mineralogical properties of brown podzolic soils in South New England, Paxton and Merrimac Series, Soil Sci. 81:287-300.
- Tamura, T. (1957). Identification of the 14 Å clay mineral component. Am. Min. 42 : 107-10.
- Tamura, T. (1958). Identification of clay minerals from acid soils. J. Soil Sci. 9: 141-47.
- Tate, K.R. and Churchman, G.J. (1978). Organo-mineral fractions of a climosequence of soils in New Zealand tussock grasslands. J. Soil Sci. 29(3): 331-39.
- *Theng, B.K.G. (1972a) . Fomation, properties and practical applications of clay- organic complexes.J. Royal Soc. of New Zealand 2: 437-57.
- Thornton, R.H., Cowie, J.D. and McDonald, D.C. (1956). Mycelial aggregation of sand soil under Pinus Radiata. Nature London 177 : 231-32.
- *Turchenek, L.W. and Oades, J.M. (1974). Size and density fractionation of naturally occurring organomineral complexes. Transactions 10th Int. Cong. Soil sci. II : 65-72.
- Tweneboah, C.K., Greenland, D,J. and Oades, J.M. (1967) . Changes in charge characteristics of soils after treatment with 0.5 M calcium chloride at pH 1.5. Aust. J. Soil Res. 5 : 247-261 .
- *Tyulin, A.F. (1937) . Composition and structure of soil organo-mineral gels and soil fertility. Trans. Conf. on Soil Sci. and Physiology of Cultivated Plants. Vol. 1, Sel'Khozgiz.

- Tyulin, A.T. (1938). The composition and structure of soil organo mineral gels and soil fertility. Soil Sci. 45 : 343-57.
- *Tyurin, I.V. (1937) . Soil organic matter. Sel'Khozgiz.
- *Ubogov, V. (1978). The effect of iron and aluminium on peptization of the humus-clay complex. Nanchnye Trudy Omskogo Sel' Skokozyaistvennogo Instituta. 171 : 36-40.
- *Valla, M., Guckert, A. and Jacquin, F. (1972). Complex fomation between montmorillonite and humic acids. I. Effect of cations on the adsorption mechanisms of 14-C humic acids. Bull. de l'Ecole Nationale Superieure d'Agronomie et des Industries Alimentaries 14(2) : 227-38.
- Van Reeuwijk, L.P. and de Villiers, J.M. (1968). Potassium fixation by amorphous aluminosilica gels. Proc. Soil Sci. Soc. Am. 32 : 238-40.
- *Vasil'eva, A.A. (1958) . Use of ultrasound in the determination of colloidal substances in clay soils.
 Sb. nauchissled. Inst. Osnovanii podzem. Sooruzh., Akad. Stroff Arkhitekt. USSR No. 30 : 49-56.
- *Vinogradov, M.A. (1942) . Pedology 3-4 : 79.
- *Vladimirov, V .E. (1968) . Study of the effect of vibrations on the physico- chemical properties of a soil suspension. Soviet Soil Sci. 5 : 654-59.
- Wada, K. and Greenland, D.J. (1970). Selective dissolution and differential infra-red spectroscopy for characterisation of amorphous constituents in soil clays. Clay Min. 8 : 241-254.
- Wada, Koji and Teruo, Higashi (1976). The categories of aluminium- and iron-humus complexes in ando soils determined by selective dissolution. J. Soil Sci. 27: 357-68.
- *Walker, G.F. (1958) . On the differentiation of vermiculites and smectites in clays. Bull, Clay Miner.3: 154-63.
- Wang, S.C., Li, S .W. and Ferng, Y.I. (1978) . Catalytic polymerization of phenolic compounds by clay minerals. Soil Sci. 126(1): 15-21.
- * Watson, J.R. (1970) . Studies of clay-organic nitrogen complexes in soils. Ph.D. Thesis, Univ. of Aberdeen. Watson, J.R. (1971) . Ultrasonic vibration as a method of soil dispersion. Soils and Ferts. 34(2) : 127-34.
- Watson, J.R. and Parsons, J.W. (1974). Studies of soil organo-mineral fractions. I. Isolation by ultrasonic dispersion. J. Soil Sci. 25 : 1-3.
- Weiss A. (1959). Cation exchange of kaolinite . 2. anorg. allgem. Chem. 297: 257-86.
- *Weissler, A., Cooper, H.W. and Snyder, S. (1950) . Chemical effect of ultrasonic waves : oxidation of potassium iodide solution by carbon tetrachloride. J. Am. Chem. Soc. 72: 1769-75.
- *Wetzel, W. (1951). Proc. Third Int. Cong. Sedimentology Groningen-Wageningen.
- White, Joe, L. (1971). Interpretation of infrared spectra of soil minerals. Soil Sci. 112 : 22-31.
- *Whittles, C.L. (1923). The determination of bacteria in soil. J. agric. Sci., Camb. 13: 18-43.
- *Wilk, K. (1964) . Preliminary investigations on the formation of organo-mineral humic compounds. Roczn. glebozn. 14 : 79-83.

- *Williams, B.G. (1965). Influence of polyvinyl alcohols on the physical properties of soil aggregates. Ph.D. Thesis, Univ. of Adelaide.
- Wood, R.W. and Loomis, A.L. (1927) . The physical and biological effects of high frequency soundwaves of great intensity. Phil. Mag. VII 4 : 417-36.
- Wright, J.R. and Schnitzer, M. (1963). Metallo-organic interaction associated with podzolization. Soil Sci. Soc. Am. Proc. 27 : 171-176.
- Yariv, S., Russell, J.D. and Farmer, V.C. (1966) . Infrared study of the adsorption of benzoic acid and nitrobenzene in montmorillonite. Isr. J. Chem. 4 : 201-13.
- Yonebayashi, K., Kyuma, K. and Kawaguchi, K. (1974). Characterization of the organic matter in soil organo-mineral complexes. J. Sci. of Soil and Manure, Japan 45(9): 416-420. Cited from Soil Sci, Pl.Nutr.21: 195.
- Yoshida, M. and Nakao, Y. (1971) . Behaviour of aluminium-humic acid complexes as revealed by titration curves. J. Sci. Soil and Manure, Japan. 42(9): 333-37. Cited from Soil Sci. Pl. Nutr. 19: 332.
- Young, J.L. and Spycher, G. (1979). Water-dispersible soil organic-mineral particles. I. Carbon and nitrogen distribution. Soil Sci. Soc. Am. J. 43(2) : 324-28.

APPENDIX I

Diagnostic lattice spacings (dhkl) in A ⁰ observed in the X-ray diffractograms
of peroxide-CBD-oxalate treated coarser fractions (2-0.05 µ) of clay-organic complex from different soils

Treatment of samples						Corresponding
Mg	Mg-	K	K saturated and heated to	K saturated and	HCl	Minerals
saturated	glycerolvated	saturated	300°C	heated to 550°C		
			1. INDORE			
15.24	19.68	12.63	12.20	12.50	-	Smectite
	9.66					
	14.24	14.25	13.70	13.60		Chlorite
7.18	7.25	7.11	7.09	7.14		
4.77	4.79	4.74	1.475			
3.53	3.57	3.55	2.55	3.53	-	
10.34	10.16	10.34	10.16	10.34	10.16	Mica
5.02	4.99	5.01	4.99	5.02	4.98	
3.34	3.36	3.35	3.40	3.36	3.33	
7.18	7.25	7.11	7.09		7.20	Kaolinite
3.53	3.57	3.55	3.55		3.59	
4.27	4.27	4.27	4.027	4.26	4.25	Quartz
3.34	3.33	3.35	3.30	3.32	3.33	
			2. SIRAGUPPA			
15.24	18.60	13.19	11.40	11.40		Smectite
	9.40					
14.24	14.33	14.19	13.92			Chlorite
7.16	7.19	7.25	7.19			
4.77	4.79	4.77	4.77			
3.58	3.58	3.58	3.56			
			3. NANDYAL			
15.92	19.00	12.84	11.70	12.36		Smectite
	9.32					
10.52	10.00	10.10	10.16	10.22	10.00	Mica
4.98	5.00	5.17	4.91	5.03	5.00	
3.36	3.36	3.35	3.35	3.38	3.35	

Treatment of samples						Corresponding
Mg	Mg-	K	K saturated and heated to	K saturated and	HCl	Minerals
saturated	glycerolvated	saturated	300°C	heated to 550°C		
7.26	7.34	7.16	7.19		7.13	Kaolinite
3.59	3.59	3.59			3.60	
	4.27	4.27	4.26	4.25	4.25	Quartz
		3.20		3.32		
	I		4. MOHITNAGA	R		
14.37	14.37	14.73	14.48	14.37	-	Chlorite
7.13	7.22	7.19	7.11			
4.72	4.73	4.78	4.77		.	
3.54	3.54	3.56	3.56			
10.10	10.16	10.30	10.22	10.04	10.11	Mica
5.02	5.05	5.05	5.05	4.99	4.99	
3.33	3.41	3.35	3.35	3.34	3.33	
7.13	7.22	7.19	7.11		7.40	Kaolinite
3.54	3.54	3.56	3.56		3.56	
4.27	4.25		-		4.25	Quartz
3.25		3.21	3.25	3.19	3.23	
14.37	14.97	14.73	14.48	14.37		Interstratified
12.02	13.92	13.19	12.66	10.78		minerals
	13.04	12.81	11.41			
	12.03	11.97				
			5. KARNAL			
14.25	14.14	12.19	11.90	12.19		Vermiculite
10.10	10.78	10.84	10.28	10.28	10.16	Mica
5.01	5.03	5.02	5.01	5.03	5.01	
3.36	3.36	3.33	3.34	3.34	3.33	
7.22	7.22	7.13	7.16		7.28	Kaolinite
3.56	3.56	3.58	3.54		3.63	
						<u> </u>
4.29	4.27	4.29	7.25	4.29	4.26	Quartz
		3.33	3.33	3.24		-

Treatment of samples					Corresponding	
Mg	Mg-	K	K saturated and heated to	K saturated and	HCl	Minerals
saturated	glycerolvated	saturated	300°C	heated to 550°C		
			6. CHIKBALLAP	UR	1	
10.42	10.42	10.39	10.16	10.84	10.10	Mica
4.98	5.02	5.02	5.02	5.09	5.01	
3.36	3.32	3.36	3.36	3.38	3.33	
7.22	7.28	7.25	7.19		7.22	Kaolinite
3.60	3.60	3.59	3.58			
			7. BENTLU			
14.25	13.92	14.03	13.92	13.40		Chlorite
7.25	7.14	7.14	7.16			
4.78	4.77	4.78	4.77			
3.49	3.55	3.53	3.55			
10.28	10.10	10.16	10.10	9.98	10.10	Mica
5.05	5.02	5.01	5.04	5.01	5.01	
3.36	3.35	3.35	3.33	3.32	3.33	
7.25	7.14	7.14	7.16		7.22	Kaolinite
3.62	3.55	3.53	3.55		3.59	
4.28	4.30	- 1	4.30		4.30	Quartz
				3.24	3.33	
14.25	13.92	14.03	13.92	13.39		Interstratified
12.27	12.63	12.54	12.27	12.72		minerals
11.63	11.71	11.12		11.78		
10.98	11.41			11.08		
			8. NADDI			
14.30	18.80	12.40	12.20	12.36		Smectite
14.30	14.37	14.25	13.60	14.03		Chlorite
7.22	7.26	7.25	7.20	7.20		
4.78	4.75	4.64	4.75			
3.59	3.59	3.60	3.58	3.59		
10.22	10.16	10.22	10.10	10.10	10.16	Mica
5.01	5.01	5.06	4.99	5.01	5.01	
		1				

Treatment of samples						Corresponding
Mg	Mg-	K	K saturated and heated to	K saturated and	HCl	Minerals
saturated	glycerolvated	saturated	300°C	heated to 550°C		
3.36	336	3.34	3.34	3.35	3.33	
7.22	7.26	7.25	7.20		7.22	Kaolinite
3.59	3.59	3.60	3.58		3.59	
4.26	4.27	4.30	4.26	4.28	4.28	Quartz
3.3.6	3.36	3.33	3.34	3.35	3.33	
14.30	14.37	14.25	13.59	14.03		Interstratified
12.81	12.63	12.63	12.83	12.03		minerals
12.28	11.55	11.94	11.87			
11.48						
			9. PALAMPUR			
14.25	14.49	14.14	13.92	14.30		Chlorite
7.15	7.15	7.14	7.11	-		
4.78	4.75	4.74	4.71			
3.56	3.56	3.54				
10.22	10.19	10.16	10.10	10.16	10.16	Mica
5.05	5.01	4 93	5.00	5.03	5.02	
3 37	3 37	3 35	3.35	3 35	3 39	
	0.07				0.07	
7.15	7.15	7 14	7 11		7 19	Kaolinite
3 56	3 56	3 54	/.11		3.58	Ruomine
5.50	5.50	5.54	-		5.50	
1 29	1 29		1 25	1 27	1 23	Quartz
3.37	3.36	3 35	3 35	3.27		Quartz
5.57	5.50	5.55	5.55	5.27		
14.25	14.49	14.14	13.02	14 30		Interstratified
12.40	12 20	12.50	13.32	11.05		minerals
13.49	13.29	11.12	11.96	11.95		minerais
11.95	12.90	10.52	10.72			
	12.54	10.53	10.72	-		
	11.91					
			10 100000			
1 4 ==		4 4 4 4 4	10. KOHIMA		1	
14.73	14.68	14.48	13.04	14.03		Chlorite
7.14	7.17	7.15	7.11			
	4.78	4.76	4.72			

Treatment of samples						Corresponding
Mg	Mg-	K	K saturated and heated to	K saturated and	HCl	Minerals
saturated	glycerolvated	saturated	300°C	heated to 550°C		
3.54	3.54	3.56	3.55			
10.00	10.00	10.30	10.30	10.14	10.28	Mica
5.01	4.98	5.06	4.99	5.01	4.99	
3.37	3.37	3.37	3.36	3.35	3.55	
7.14	7.17	7.15	7.11		7.19	Kaolinite
3.54	3.54	3.56	3.55		3.52	
4.29	4.29	4.34	4.27		4.29	Quartz
3.36	3.37	3.24	3.36	3.25	3.35	
14.73	14.68	14.48	13.03	14.03		Interstratified
12.90	13.09	12.81	11.63	11.19		minerals
12.27	12.45	11.86	10.91			
11.48	11.71	11.08				
			11. JORHAT			
14.37	14.49	13.70		13.49		Chlorite
7.22	7.25	7.22	7.25			
4.78	4.80		4.78			
3.54	3.60	3.59	3.60			
10.27	10.16	1010	10.22	1019	1010	Mica
4.92	5.04	5.02	5.01	5.08	5.01	
3.32	3.36	3.36	3.34	3.40	3.33	
7.22	7.25	7.22	7.25		7.19	Kaolinite
3.54	3.60	3.59	3.60		3.59	
14.37	14.48	13.70	12.86	13.49		Interstratified
12.61	12.41	12.36	11.33	11.86		minerals
12.19	11.08	11.71		11.71		
11.41		10.53				
			12. TAMANDA			
13.81	13.81	14 60	13.60	12.27		Chlorite
7 22	7 25	7 33	7 22			Chionic
1.22	1.23	1.55	1.22			

Treatment of samples						Corresponding
Mg	Mg-	K	K saturated and heated to	K saturated and	HCl	Minerals
saturated	glycerolvated	saturated	300°C	heated to 550°C		
3.59	3.59	3.59	3.66			
10.10	9.99	10.10	10.16	10.72	10.04	Mica
5.01	5.01	5.01	4.98	5.03	5.01	
3.47	3.36	3.36	3.33	3.36	3.33	
7.22	7.25	7.33	7.22		7.20	Kaolinite
3.59	3.59	3.59	3.66		3.57	
4.27	4.26	4.29	4.27		4.29	Quartz
			3.25	3.24		
13.81	13.81	14.60	13.59	12.27		Interstratified
13.09	12.36	13.39	11.63	11.63		minerals
12.63	11.40	12.63				
11.78	10.43	11.40				
11.05						
			13. HENNINGKONG	JLWA		
14.44	14.14	13.81		14.02		Chlorite
7.28	7.14	7.14	7.20			
4.77	4.76	4.75		4.56		
3.54	3.54	3.54	3.59			
10.34	10.52	10.18	10.25	10.09	10.16	Mica
5.05	5.01	5.02	5.01	5.08	4.98	
3.36	3.36	3.36	3.36	3.38	3.33	
7.28	7.14	7.14	7.20		7.13	Kaolinite
3.57	3.57	3.55	3.59		3.59	
4.27	4.27	4.28	4.27	4.30	4.27	Quartz
				3.27		
14.44	14.14	13.81	12.63	14.02		Interstratified
11.78	12.36	13.20		12.63		minerals
11.51	11.22					
	10.52					
	-					
			14. KATWA			
1						

	Corresponding					
Mg	Mg-	K	K saturated and heated to	K saturated and	HCl	Minerals
saturated	glycerolvated	saturated	300°C	heated to 550°C		
14.73	18.03	12.66	12.40	12.30		Smectite
14.73	13.29	13.00	14.02	14.70		Chlorite
7.25	7.36	7.19	7.14			
4.77	4.80	4.79				
3.56	3.56	3.55	3.56			
10.24	10.32	10.22	10.04	1010	10.10	Mica
5.05	5.06	5.05	5.01	5.05	5.03	
3.35	3.37	3.36	3.35	3.34	3.33	
7.25	7.36	7.19	7.14	Ŧ	7.14	Kaolinite
3.60	3.61	3.59	3.56		3.57	
14.73	15.24	14.14	14.03	14.70		Interstratified
13.70	13.29	13.39	12.45	13.70		minerals
12.50	12.63	12.63	11.77	11.86		
	11.63	11.63	11.10	11.12		