Soil Mineralogy and Clay Minerals

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Abstract

Soil mineralogy indicates primarily the parent materials from which the soil has developed. It also translates valuable information regarding the past climatic conditions and how the transition from past to present day climate occurred. This chapter highlights the physical phenomena like swelling and shrinkage, aggregation and thixotropy as strongly related to the mineralogical composition of soils. Similarly, chemical phenomena like adsorption and desorption of heavy metals (e.g. Zn, Cd, Pd etc.), and fixation of P and K depend on a great extent on soil mineralogy, especially clay mineralogy. Clay minerals form bonds of varying strengths with soil humus resulting in clay-humus complexes of varying stability. Distribution of non-labile and labile C in soil is also closely related to the different clay minerals present in soil. Such relations of clay minerals with soil organic matter have great implications on soil C-sequestration. The clays and clay minerals are not only the integral part of soils but also the driving factors in the dynamics of edaphology and pedology. The chapter covers different aspects of mineralogy of Indian soils based on the studies conducted since the 1950s to till date. Information on the mineralogical compositions of all the major soil groups of India has been presented. Efforts are made to link soil mineralogy with pedogenesis and climate. Some site-specific soil features related to soil mineralogy, e.g. effect of zeolites on fertility of calcareous Vertisols, presence of dioctahedral smectites in ferruginous Alfisols, spatial association of red and black soils, interstratification of kaolinite with smectite at some sites have been documented. Thereafter, the impact of soil minerals on different soil physical and chemical properties followed by the interaction of clay minerals with humus and different pesticides and other soil pollutants have also been established. The chapter ends with the findings of some advanced studies on soil mineralogy as carried out by Indian researchers.

Keywords

Soil mineralogy • Clays and clay minerals • Amorphous minerals • Pedogenesis • Clay-humus interaction

6.1 Introduction

In India, the study on soil mineralogy started with the use of X-ray diffraction technique for identification of clay minerals in soil in 1951 by Bagchi under the guidance of Prof. J. N. Mukherjee in the laboratory of Prof. S. N. Bose at Dacca (now in Bangladesh). The X-ray instruments at that time were much less sophisticated than they are today. A large number of Indian soils were analysed in H-saturated condition by Bagchi (1951). He showed that laterite soil contained kaolinite and quartz; black cotton soil from Satara and Mumbai contained montmorillonite; red earth from Coimbatore taluk contained kaolinite and quartz. After that, Das (1956) made an X-ray identification of soil clays isolated from black cotton soils of Indore, brown Matasi soil of Labhandi and alluvial soils of Delhi and Karnal. He found montmorillonite with small amounts of kaolinite and traces of illite in the black cotton soil clays; mainly illite and kaolinite in the brown Matasi soil clays; and illite with small amounts of kaolinite in the Delhi and Karnal soil clays. One year later, Adhikari (1957) reported the presence of illite and small amounts of kaolinite in some soils of West Bengal. Hence, mineralogical research in India initiated in the 1950s. For first few decades after initiation, researchers in India

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mainly tried to find out the distribution of different minerals in various Indian soils in general, and in the clay fractions of the major soil groups of India in particular. Presently, the applied aspects of mineralogy are gaining more importance.

6.2 Distribution of Clay Minerals in Major Soil Groups of India

Percentage distribution of different clay minerals in different soil groups of India based mainly on X-ray diffraction studies has been discussed in this section.

6.2.1 Alluvial Soils

Alluvial soils cover around 75 Mha area across India and mainly occur in the Indo-Gangetic Plains, Brahmaputra valley and the coastal and deltaic regions (Seghal 1996). States of Delhi, Punjab, Uttar Pradesh, Haryana, West Bengal, Bihar, Assam, Orissa, Tamil Nadu, Kerala, Andhra Pradesh and Gujarat show the presence of alluvial soils. Studies by Pundeer et al. (1978) in some soil profiles of central Punjab revealed the dominance of illite (37–66%) in the clay fraction. The same also contained kaolinite (10–26%), chlorite (15–18%), vermiculite (4–18%), smectite (2–13%), hydrobiotite and metahalloysite. Besides this, alluvial soils of Lakhimpur in Assam; of Cooch Behar, Mursihidabad, Hoogly, Howrah, Nadia and Burdwan districts of West Bengal; of Patna, Katihar, Sabour, Saharsa, Araria and Rexaul of Bihar have illite as the dominant clay mineral (Adhikari 1957; Prasad et al. 1967; Datta and Das 1972; Ghosh and Datta 1972). Soils of Delhi, Haryana and Punjab showed illite as the dominant mineral, which was associated with kaolinite, chlorite, montmorillonite and some mixed layer minerals (Das 1956; Ghosh 1964; Singh et al. 1972). Some researchers (Sehgal and Coninck 1971) reported that the chlorite found in Punjab, Haryana and Himachal Pradesh was actually chloritized vermiculite or montmorillonite; only the Hapludolls and Hapludalfs of Punjab contained true chlorite. Alluvial soils of Jammu and Kashmir also showed the dominance of illite in the clay fraction (Gupta 1967). Udaipur alluvial soils were also illitic but contained appreciable quantities of chlorite and quartz (Khangarot et al. 1972). Alluvial soils from Rupnagar of Punjab (Verma et al. 1994), and Karnal, Faridabad and Rohtak of Haryana (Ravi Kumar et al. 1991) were found to be predominantly illitic with contents ranging from 36 to 61% at different sites. Some calcareous alluvial soils from Bihar showed the dominance of illite in combination with kaolinite and chlorite (Ghosh 1964; Das and Datta 1969). Clay minerals in Alfisols occurring in Siwan district of north Bihar were almost identical to the clay minerals of most of the alluvial soils of Bihar (Mall and Mishra 2000). Mishra and Ghosh (2000) presented a detailed identification of clay types in mica-rich soils of Bihar and Jharkhand. Mishra et al. (1996) presented a map of Bihar (including Jharkhand) showing clay mineral associations, which needs refinement. The clay minerals in soils of Rajmahal Trap of Jharkhand were also identified in toposequences with red, yellow and red soils (Tiwary and Mishra 1992a, b, 1993). Soils of deltaic alluvium of Canning in West Bengal recorded illite to the tune of 40% of clay fraction, followed by smectite (30%), chlorite (15%), mixed-layer minerals (10%) and kaolinite (5%) (Ghosh and Datta 1972). The *Tal* land soils of Bihar are typical showing vertic features (*Udic Chromustert*) in south of the Ganga alluvium (Tiwary and Mishra 1990).

Illite is not the most dominant mineral in all the alluvial soils. Alluvial soils in many parts of West Bengal showed the dominance of smectite (30–60%) in the clay fraction, followed by mica (10–40%), chlorite (5–40%), mica-smectite or mica-vermiculite mixed-layer minerals (5–20%), kaolinite (6–10%) and a little amount of quartz (Ghosh and Datta 1974; Ghosh et al. 1974, 1976). Soils from different parts of Nadia, Hoogly and Burdwan districts of West Bengal have been found to be dominated by montmorillonite, with the presence of mixed-layer minerals and chlorite (Ghosh and Datta 1972; Ghosh et al. 1972; Ghosh 1973). Sand, silt and clay fractions of four benchmark soils (Ballartop, Chandipur, Narayanpur and Patibunia) occurring on the coastal plains in West Bengal were studied to identify the minerals present in these fractions and also to understand their transformation in the ecosystem (Nayak and Sarkar 2013). Clay fraction of some heavy-textured soils from Patna and Bhagalpur showed the presence of montmorillonite, vermiculite, illite and a few unrecognized minerals. Among them, some contained more montmorillonite than vermiculite, and some had more vermiculite than montmorillonite. Most of the soil clays from Bharatpur and Jaipur showed the dominance of montmorillonite (Khangarot et al. 1972). Some of the alluvial soils also show the dominance of kaolinite in the clay fraction. Soils from Sibsagar of Assam were dominantly kaolinitic with small quantities of illite and quartz (Das and Datta 1969). Sen and Chatterjee (1960, 1963) observed the dominance of kaolinite in pre-monsoon Gangetic silt.

6.2.2 Red Soils

Red soils, sometimes along with lateritic soils, mainly occur in Andhra Pradesh, Tamil Nadu, Maharashtra, Karnataka, Kerala, Goa, Orissa, West Bengal and north-eastern states of India. Red soils are usually of kaolinitic dominance, but sometimes illite and rarely montmorillonite can also become the dominant mineral in the clay fraction. In West Bengal, red soils of Midnapur and Bankura were found to be dominantly kaolinitic (50–55%), with the presence of illite (25–35%), smectite (10–15%), chlorite (0–5%) and mixed-layer minerals (0–5%) (Ghosh et al. 1974). Red soils in Burdwan district of West Bengal also dominantly contained kaolinite (42%), with as high as 30% illite and 17% smectite (Ghosh and Das 1976). Kaolinite contents in red soils of Kerala and Karnataka were as high as 90%. In a study conducted by Bhattacharyya and Ghosh (1990), on red soils derived from granite-gneiss in Bangalore revealed that kaolinite content (48–77%) decreased, while mica content (23–32%) increased down the profile. In the same profiles, smectite was absent in A and B horizons but was present in the C horizon. Red sandy soils of Ganjam, Balasore, Kalahandi, Puri and Koraput districts of Orissa were mainly dominated by kaolinite with some illite content (Das 1972; Datta and Adhikari 1972; Sahu and Nanda 1972). Clay fractions of the red soils from different parts of Bihar were also dominated by kaolinite with considerable amounts of illite (Ghosh and Das 1963; Sinha and Mandal 1963). However, genesis of red soils in Rajmahal Trap and other parts especially in Jharkhand were earlier studied in detail (Tiwary et al. 1987, 1996, 1997; Singh and Mishra 1995).

The loamy textured red soils of Maldah district of West Bengal showed preponderance of illite (60%) along with mixed-layer minerals (20%), chlorite (15%) and kaolinite (5%) (Ghosh and Datta 1972). Similar soils from Orissa also showed dominance of illite in association with kaolinite and montmorillonite (Sahu and Nanda 1972). In Mysore, the red sandy soils are illite dominant with the presence of some kaolinite (Ramkrishnaya 1971). Red and yellow soils in some parts of Tripura, Bihar and Orissa have been reported to contain illite as the most important mineral followed by kaolinite and sometimes chlorite (Singh and Sinha 1972; Ghosh 1973).

6.2.3 Black Soils

Black soils are mostly dominated by smectitic minerals; however, illite may also be present sometimes as the dominant mineral. Black soils present in the basaltic regions of Madhya Pradesh were recorded with 60–78% smectite along with 7–12% kaolinite and 5–12% illite (Chatterjee and Rathore 1976). Apart from montmorillonite and illite, some kaolinite was also detected in soil clays of Guntur and Lam in Andhra Pradesh (Ramkrishnaya 1971). Rao et al. (1983), after studying eight pedons from semiarid regions of Andhra Pradesh reported that clay fraction of soils developed from limestones and buff shales was smectite dominant. They also observed that black soil of Vertisol order contained at least 50% smectite apart from 21 to 30% mica and 6–10% chlorite and kaolinite. Shallow black soils developed on basaltic parent material in Chindwara of Madhya Pradesh revealed the dominance of illite in the clay fraction. Apart from illite, an appreciable quantity of montmorillonite, illite-montmorillonite mixed layer and 2:1–2:2 intergrade minerals were also present (Ghosh 1964). Dubey et al. (1985) studied the mineralogy of different mechanical separates in sodic Vertisols of western Madhya Pradesh. They observed that the fine sand fractions contained 95–97% of light minerals, mainly in the form of feldspars and quartz. In the silt fraction, albite was the major mineral followed by anorthite. In the clay fraction, smectite was the dominant mineral constituting 58–64%.

6.2.4 Laterite Soils

Laterite soils are mainly observed in the southern, south-eastern and north-eastern states covering an area of about 40 Mha (Seghal 1996). The most dominant clay mineral in laterite soils is kaolinite. Apart from kaolinite, presence of illite, chlorite, montmorillonite, vermiculite, quartz and feldspars has also been reported. Laterite soils of Midnapur and Bankura districts in West Bengal were found to be dominant in kaolinite with contents in clay ranging from 49 to 60%. Along with kaolinite, 20–29% mica, 7–20% mixed layer, 4–7% smectite, and 4–7% chlorite were also present (Ghosh and Datta 1974; Ghosh et al. 1974). In some parts of Midnapur, laterite soils showed the dominance of illite (60–70%) with kaolinite as the second dominant mineral (25–35%) and a little amount of quartz (5%). Laterite soils of Belgaum were dominant in kaolinite (50–88%) in association with chlorite (5–10%), illite (0–10%), smectite (3–5%), and tectosilicates like quartz (3–15%) and feldspars (4–10%) (Datta et al. 1973). Apart from kaolinite as the main clay mineral, Ghosh and Tomar (1973) reported the presence of diatom skeletons in laterite soils of Kadoli (Belgaum). Clays of laterite soils from Kerala were reported to contain kaolinite and halloysite as the principal minerals (Datta and Das 1972). Gibbsite as a component of soil clays was present in areas with high and excessive rainfall but not in low rainfall areas (Gowaikar 1972).

6.2.5 Hilly Soils

Hilly soils have a number of different minerals in the clay separates. In soils of Palam valley, the clay fractions contained illite (18–44%), chlorite (17–28%), vermiculite (6–19%), mixed-layer minerals (18–42%) and smectite (7–38%) (Gupta and Tripathi 1988). Clays in hilly soils of Kangra district showed the presence of illite (25–45%), smectite (0–35%), kaolinite (0–25%), chlorite (10–35%), vermiculite (0–25%) and mixed-layer minerals (15–35%) (Gupta et al. 1991). The same workers found 20–50% illite, 10–50% chlorite and 10–50% smectite in some soils from Poonch and Rajouri of Kashmir.

6.2.6 Tarai Soils

Tarai soils found in the northern parts of West Bengal are dominantly illitic (45–55%), with substantial quantities of chlorite (25–40%). Other minerals like mixed layer (5–20%), kaolinite (5%) and quartz (5%) are also present (Ghosh and Datta 1972). Tarai soils of Nainital district of Uttar Pradesh (UP) are similar in mineralogy to those found in West Bengal (Ghosh 1964). Some tarai soils have regular interstratification of mica-vermiculite in the soil clay fraction (Sahu et al. 1977; 1981).

6.2.7 Saline and Alkali Soils

Ghosh and Datta (1974) studied the coastal soils of West Bengal and reported the presence of illite (45%), smectite (25%), vermiculite (10%), chlorite (8%) and kaolinite (5%). Predominance of illite and kaolinite was observed in saline-alkali soils of Lucknow, UP (Raychaudhuri 1952–1953). Some saline soils have been reported to contain sepiolite (Kanwar 1959; 1961). Pandey and Pathak (1972) observed the presence of mica-montmorillonite and vermiculite-chlorite interstratified minerals in the salt-affected soils of Kanpur, UP.

6.2.8 Peaty Soils

Studies in peaty soils from Varanasi, UP revealed the presence of montmorillonite and kaolinite in the clay fraction (Rao 1963). Investigation on acid sulphate soils of Kerala by Ghosh et al. (1973) and Ghosh and Tomar (1973) revealed that kaolinite along with halloysite formed 34–37% of the clay. Apart from these two, smectite (18–32%), illite (6–12%), chlorite (4–11%), vermiculite (0–5%), interstratified minerals (4–12%), gibbsite (6–17%), amphibole (0–4%), quartz (0–2%) and feldspars (0–2%) were also present.

6.3 Amorphous Clay Minerals in Soil

Amorphous minerals mainly occur as coatings on crystalline minerals and are very difficult to separate. However, these can be selectively dissolved. First systematic study of amorphous minerals in Indian soils has been carried out by Krishna Murti et al. (1976). The amorphous minerals selectively dissolved from clay fraction of twenty-six ferruginous soils contained considerable amounts of iron (Fe) in addition to silicon (Si) and aluminium (Al). They termed these as amorphous ferri-aluminosilicates (AFAS) having silica (SiO_2): alumina (Al_2O_3) and SiO_2: sesquioxides (R_2O_3) molar ratio varying from 2.03 to 3.52 and 1.72 to 2.95, respectively. The model of AFAS postulated by them consisted mainly of negatively charged tetrahedrally coordinated silica-alumina phase, $Si_3AlO_6(OH)_4$ containing domains of neutral FeOOH with an outer positively charged hydroxyl-aluminium polymeric component $[Al(OH)_{2.5}]_n$. The calculated mean hydroxyl water content of the AFAS was 17.8%, and CEC ranged from 48.6 to 112 cmol(+) kg^{-1}. The CEC showed a high positive correlation with the ratio of the tetrahedral Si–Al component to the octahedral Al and a high negative correlation with the outer hydroxyl-aluminium octahedral component, but the same had no relationship with the Fe content. The amount of AFAS ranged from 19 to 32% in the clay fraction. They postulated that these AFAS formed preceding the formation of kaolinite in these soils. Initially, the soil solution was rich in bases and high in pH which favoured the tetrahedral coordination. The Fe was the first to precipitate and form colloidal solution on which chemisorption of Si took place which stabilized the amorphous state of Fe-particles. Then solution tetrahedral Al got incorporated in Si-network so that a tetrahedrally coordinated Si–Al gel structure was obtained. The Fe formed the domains in this three-dimensional mass. With time as leaching continued, formation of octahedrally coordinated polymeric hydroxyl-aluminium ions took place, which got attached electrostatically to the negatively charged Si–Al phase and neutralized the negative charges. Another consequence of lower pH is the tendency of Al to change its coordination from four to six which would favour the crystallization of kaolinite. The crystallization of kaolinite from Si–Al gel is very slow, but the presence of Fe domains in this gel mass caused loss of stability of tetrahedrally coordinated Al. In fact, the kaolinite minerals in these soils contained lots of Fe in octahedral layer (Rengasamy et al. 1975a, b).

Considerable amounts of amorphous materials were reported in the clay fraction of laterite soils of Madhya Pradesh (Gaikwad and Govindarajan 1971); in arid soils of Rajasthan (Choudhari and Dhir 1983); in Vertisols (Seshagiri Rao et al. 1992); in soils derived from mica-rich parent materials of Bihar (Mishra and Ghosh 1994); and alluvium-derived soils of Assam (Karmakar and Borah 1996). Karmakar (2012) studied the AFAS in five soils from Assam's lower Brahmaputra valley, namely Ruptic-Ultic Dystrudepts (P1) developed on lower piedmont plain, Aquic Udipsamments (P2) developed on alluvial fan plain, Umbric Dystrudepts (P3) developed on alluvial plain, Oxyaquic Udifluvents (P4) developed on flood plain and Typic Hapludults (P5) developed on monadnock. The clay fraction of these five soils contained 10.14–38.16% AFAS with SiO_2: R_2O_3 ratio of 0.99–2.69 and SiO_2: Al_2O_3 ratio of 1.05–3.18 (Table 6.1). The P5 soils showed the largest amount of AFAS (30.67–38.16%), and the P1 soils had the lowest of AFAS (10.14–12.39%). In the P1 and P5 soils, the Bt

Table 6.1 Amorphous ferri-aluminosilicate minerals in the clay fractions of five different soils from Assam's lower Brahmaputra valley (Karmakar 2012)

Horizon	Neutral FeOOH (*a*)	Tetrahedral $Si_3AlO_6(OH)_4$ (*b*)	Octahedral $Al(OH)_2$ (*c*)	Hydroxyl water	Amorphous material (*a* + *b* + *c*)
	% of soil clay				
P1: Lower piedmont plain (Kochugaon): Ruptic-Ultic Dystrudept					
A	1.29	6.33	2.52	1.81	10.14
BA	1.23	6.67	2.88	1.96	10.78
Bt	1.47	7.08	3.84	2.30	12.39
BC	1.26	6.40	4.22	2.27	11.88
P2: Alluvial fan plain (Gossaigaon): Aquic Udipsamment					
Ap	1.33	10.09	1.52	2.14	12.94
AC	1.57	8.20	2.27	2.08	12.04
C1	3.03	7.82	2.14	2.13	12.99
P3: Alluvial plain (Bhaoraguri): Umbric Dystrudept					
A1	1.39	9.94	4.48	2.93	15.81
A2	1.57	9.40	4.56	2.87	15.53
Bw	1.08	6.90	6.70	2.99	14.68
2C1	1.27	10.09	11.95	4.91	23.31
2C2	1.71	8.69	8.42	3.80	18.82
P4: Flood plain (Khoraghat): Oxyaquic Udifluvent					
A1	0.93	9.77	2.29	2.25	12.99
A2	1.01	9.11	2.03	2.09	12.15
2C1	1.51	5.98	5.41	2.53	12.90
2C2	1.08	8.07	5.56	2.88	14.71
3C3	1.77	10.32	6.05	3.43	18.14
P5: Monadnock (Alamganj): Typic Hapludult					
Ap	1.54	22.15	6.98	5.56	30.67
BA	1.65	23.92	8.71	6.32	34.28
Bt1	2.19	26.39	9.58	6.97	38.16
Bt2	2.29	26.07	9.74	7.00	38.10

horizons had the highest content of AFAS within the entire profile. Tetrahedral $Si_3AlO_6(OH)_4$ component followed by octahedral $Al(OH)_{2.5}$, and FeOOH components mainly constituted the AFAS in the studied soils. The AFAS of the five soils contained 16.4–21.1% (mean, 18.5%) of hydroxyl water, and its variation was very narrow (18.1–18.4%) in Typic Hapludults (P5), which were more developed.

Mineralogy of soil samples collected from different depths of two A-C pedons from two different altitudes of Darjeeling Himalayan region was investigated by CEC determinations, thermogravimetric analysis and selective dissolution analysis (Sahu and Patra 1985). Content of AFAS minerals in the soil clay fractions, determined from Si, Al, and Fe extracted by 0.5 N NaOH, ranged from 12.4 to 21.6% with SiO_2: R_2O_3 molar ratios of 4.54–7.16 and 2.77–5.40 at two sites. Clay fractions were mainly rich in mica and chlorite with good amounts of kaolinite and AFAS. Mica and chlorite in the soil clays inherited from the schists, gneisses and slates present in the parent rocks. Presence of AFAS was due to adsorption of silicic acid monomers on precipitated Fe-hydroxide colloids along with the formation of silica-alumina gel structure in earlier alkaline environment by cross linking. Kaolinite was proposed to be formed from AFAS by crystallization upon ageing. Weathering mean was also calculated for soil clays of different horizons of both the profiles. Frequency distribution of clay minerals of different depths in both the pedons was more or less similar and gave three peaks at 7th, 9th and 11th stages of weathering.

Chatterjee et al. (2015), from an investigation on some Indian soils, concluded that formation or dissolution of short-range order minerals by low molecular weight organic acid depends on the concentration of the acid. They observed that citric acid concentration of 20 mg L^{-1} led to the formation of maximum amount of oxalate extractable allophane

+imogolite and total oxides of colloidal clay in Inceptisols. In Alfisols, 10 mg L^{-1} and in Vertisol, 40 mg L^{-1} citric acid concentration resulted in the highest amount of AFAS. Averaged over the three soil types, 10 mg L^{-1} of citric acid concentration led to the highest amount of AFAS. Increase in citric acid concentration resulted in decrease in crystalline iron content in colloidal clay.

In another study, Chatterjee et al. (2013) investigated the distribution and involvement of short range order minerals or AFAS in rhizosphere and non-rhizosphere zones under three different nutrient status, namely 'depleted' (soil pre-depleted with sorghum-sudan grass hybrid), 'original' (untreated) and 'fertilized' (original soil fertilized with N, P and K) in soils of three different orders (Alfisols, Inceptisols and Vertisols). In fine clay (<0.2 µm), the AFAS content (averaged across nutrient status and order) was significantly higher in rhizosphere than non-rhizosphere (Fig. 6.1a); while in coarse clay, average AFAS was more in non-rhizosphere (Fig. 6.1 b). In fine clay, Inceptisols had the highest mean AFAS content followed by Vertisols, and least content was in Alfisols. In coarse clay, Vertisol showed the highest mean AFAS content followed by Alfisols and Inceptisols. Mean content of AFAS in fine clay was more under 'original' and 'depleted' fertility status than the 'fertilized' one. Mean AFAS content in coarse clay under 'depleted' fertility was significantly higher than that under 'original' and 'fertilized' fertility status. Among the short range order minerals, mean allophane + imogolite content was highest in the fine clay of Inceptisol and coarse clay of Vertisol, while poorly ordered Fe, crystalline Fe and ferrihydrite were maximum in Alfisol. In the same study, they also investigated the non-labile carbon: labile carbon (C_{NL}: C_L) ratio, which is an index of carbon (C)-sequestration (Fig. 6.2). Higher value of this ratio indicates greater C-sequestration. It

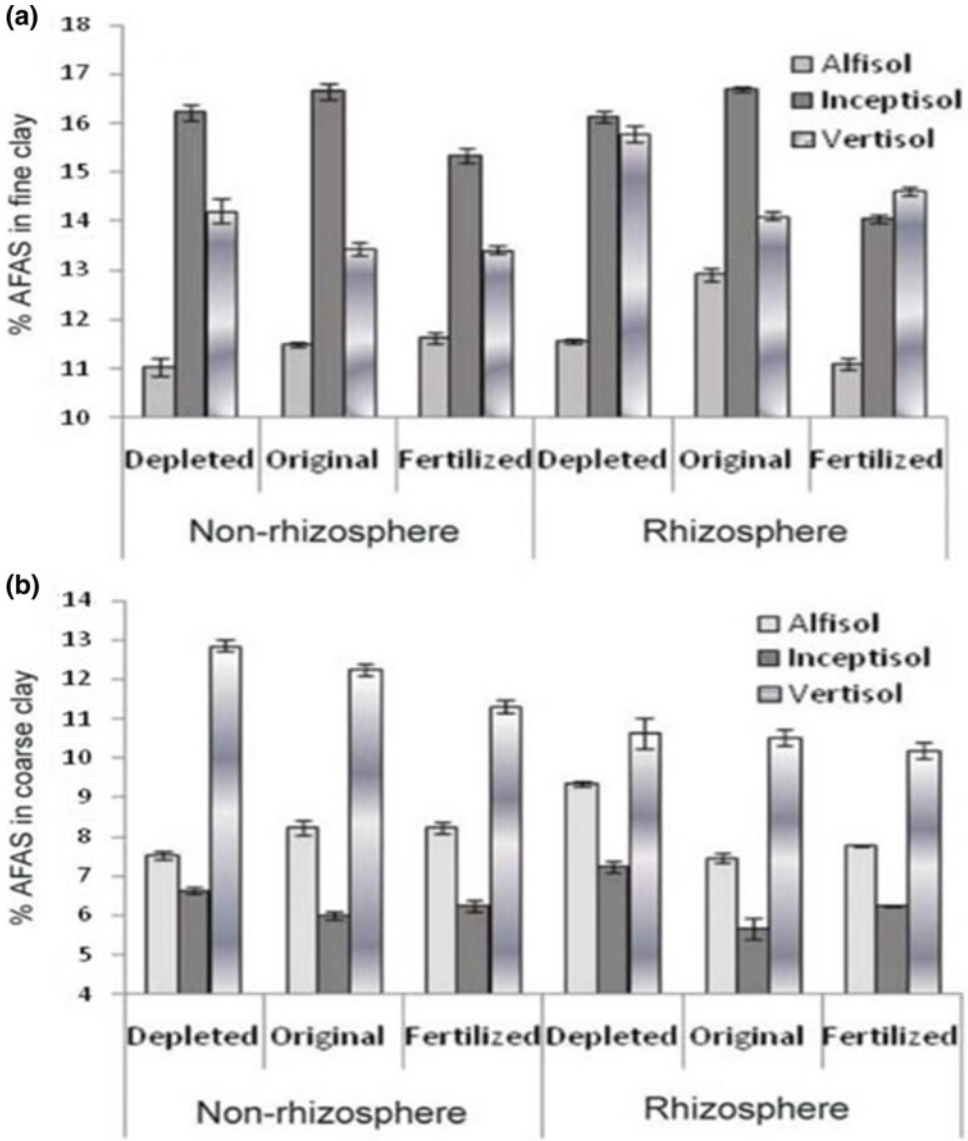

Fig. 6.1 Amorphus ferri-alumino silicate (AFAS) content (%) in **a** fine (<0.2 µm) and **b** coarse (2–0.2 µm) clay-humus complex (Chatterjee et al. 2013)

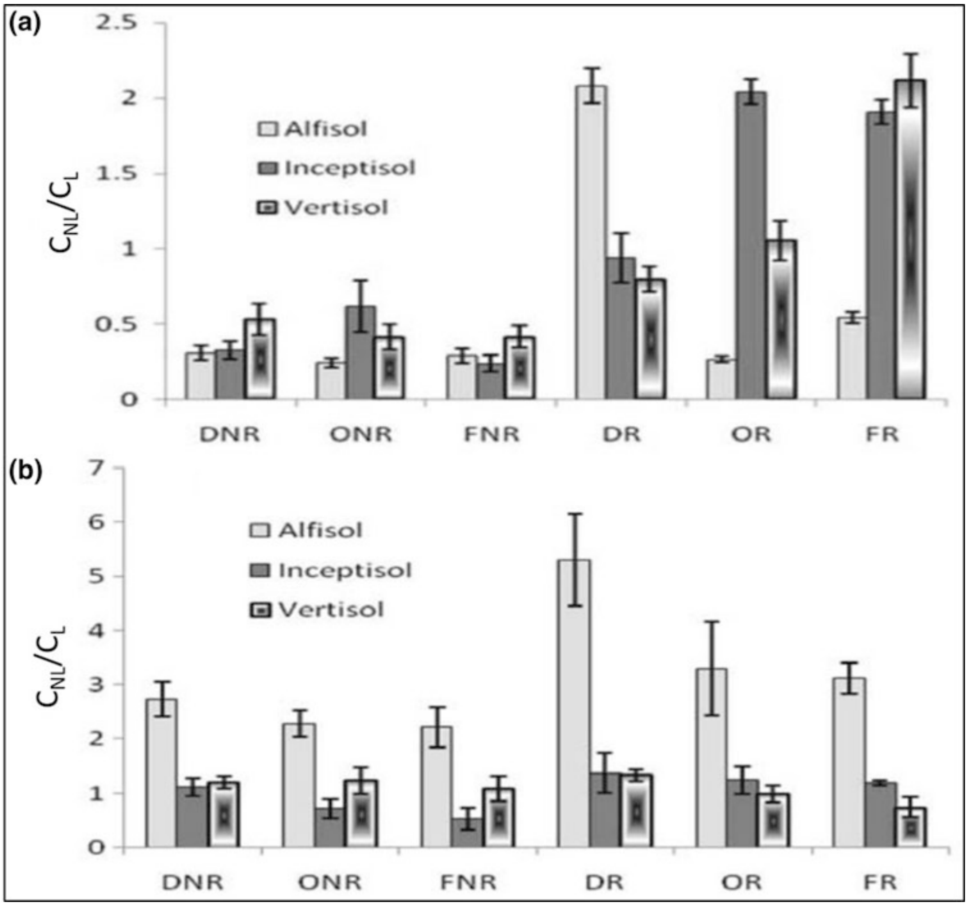

Fig. 6.2 Non-labile carbon: labile carbon (C_{NL}: C_L) ratio of **a** fine (<0.2 µm) and **b** coarse (2–0.2 µm) clay-humus complex. R-Rhizosphere; NR-Non-rhizosphere; D- Depleted; O-Original; F- Fertilized (Chatterjee et al. 2013)

was found that C_{NL}: C_L ratio for both non-rhizosphere and rhizosphere soil was more in Alfisols than Vertisols and Inceptisols. Within Alfisols, the same was significantly higher in rhizosphere soil than non-rhizosphere soil (Fig. 6.2). The content of short-range order minerals was less in Alfisols than the other two orders, but Alfisols had the highest contents of poorly crystalline Fe, crystalline Fe and organically bound Fe. Hence, organo-metallic complexes played more important role in C-sequestration than organo-mineral complexes.

6.4 Mineralogical Impacts on Pedogenesis and Soil Development

6.4.1 Linking Clay Minerals to Parent Material and Climate Change

Ram et al. (2013) studied the rate of weathering in soils evolved over sandstone, quartzite and shale landscapes from the mineralogical composition of mechanical separates of soils collected from five different physiographic divisions of Prakasam district of Andhra Pradesh. The soils belonged to Entisols, Inceptisols, Alfisols and Vertisols. They observed that mica and kaolinitic minerals mainly dominated the soils developed over sandstone and quartzite, while smectite was the dominant mineral in soils evolved from shale. Quartz, K-, Na- and Ca-feldspars and mica were the important minerals found in the sand and silt fractions of these soils. From the weathering index, they observed higher weathering rate in Vertisols than Inceptisols, Entisols and Alfisols. Alfisols showed the least rate of weathering among the four soil orders.

Several Indian researchers have considered minerals of intermediate weathering stage as potential indicators of paleoclimatic changes in parts of central India and Gangetic Plains (Pal et al. 1989; Srivastava et al. 1998; Pal et al. 2009, 2011). They have demonstrated how secondary minerals like di- and trioctahedral smectites, smectite-kaolin interstratified minerals (Sm/Kao), hydroxy-interlayered smectite (HIS), hydroxy-interlayered vermiculite (HIV), pseudo-chlorite (PCh) of intermediate weathering stage and $CaCO_3$ of pedogenic (PC) and non-pedogenic (NPC) origin can be regarded as potential indicators of paleo-climatic changes in major soil types of India. Pal et al. (2012) observed slight spatial variations in type and depth distribution of clay minerals in cores (~50 m deep) from the northern (IITK) and southern (Bhognipur) parts of the Ganga–Yamuna interfluve in the foreland basin of Himalaya, India, which they attributed to the combined effects of climatic transitions and sediment source. The core sediments from the northern part were rich in mica. Their fine clay fractions showed the dominance of dioctahedral low-charge smectites (LCS) with hydroxyl interlayering, while coarse clay and silt fractions revealed the dominance of trioctahedral high-charge smectites (HCS) (Fig. 6.3a). Low mica content was recorded in the core sediments from the southern part. In these sediments, the upper 28 m showed the presence of both LCS and HCS, while the lower part was predominantly LCS (Fig. 6.3b). The paleosols in these cores developed under semi-arid to sub-humid climates revealed the presence of 10–14 Å minerals in the clay fraction, e.g., HCS, LCS, PCh, vermiculite, hydroxyl-interlayered vermiculite (HIV) and kaolinite (formed under earlier humid condition). Large scale conversion of biotite to LCS from cratonic or Himalayan sources and interlayering by hydroxyl groups of smectite are very less likely in the alkaline soil reactions of the contemporary semi-arid climate. Hence, the presence of PCh, LCS, kaolinite and HIV points out that there has been a shift in climate in the Ganga Plains from humid to semi-arid.

The ferruginous Alfisols overlying the saprolites dominated either by dioctahedral smectite or kaolin are relict paleosols (Pal et al. 1989; Chandran et al. 2000), which have been affected by the climatic changes from humid to drier conditions during the Pliocene-Pleistocene transition period. Well-crystallized dioctahedral smectites as the first weathering product of peninsular gneiss partly transformed to kaolin in ferruginous soils (Alfisols) formed in a pre-Pliocene tropical humid climate (Pal et al. 1989). Such kaolin (Kao) is not a discrete kaolinite as XRD diagrams of its Ca-saturated and glycolated sample indicates the broad base of 0.72 nm peak and tails towards the low angle. On heating the K-saturated sample at 550 °C, the 0.72 nm peak disappears, confirming the presence of kaolin and simultaneously reinforces the 1.0 nm region at much higher degree even in presence of 1.4 nm minerals, indicating the presence of Kao-HIV/HIS (kaolin interstratified with either hydroxy-interlayered vermiculite, HIV or smectite, HIS). With the termination of humid climate, both these clay minerals were preserved to the present.

6.4.2 Spatially Associated Red Ferruginous (Alfisols) and Black (Vertisols) Soils

Occurrence of spatially associated red ferruginous (Alfisols) and black (Vertisols) soils on gneiss under similar topographical conditions is very common in semi-arid region of southern peninsular India (Pal and Deshpande 1987). Ferruginous soil clays consist mostly of kaolin and smectite, whereas black soil clays are dominated by low charge dioctahedral smectite. The inverse relation between kaolin and smectite with pedon depth of ferruginous soil clays (Pal et al. 1989) indicated the transformation of smectite to kaolin

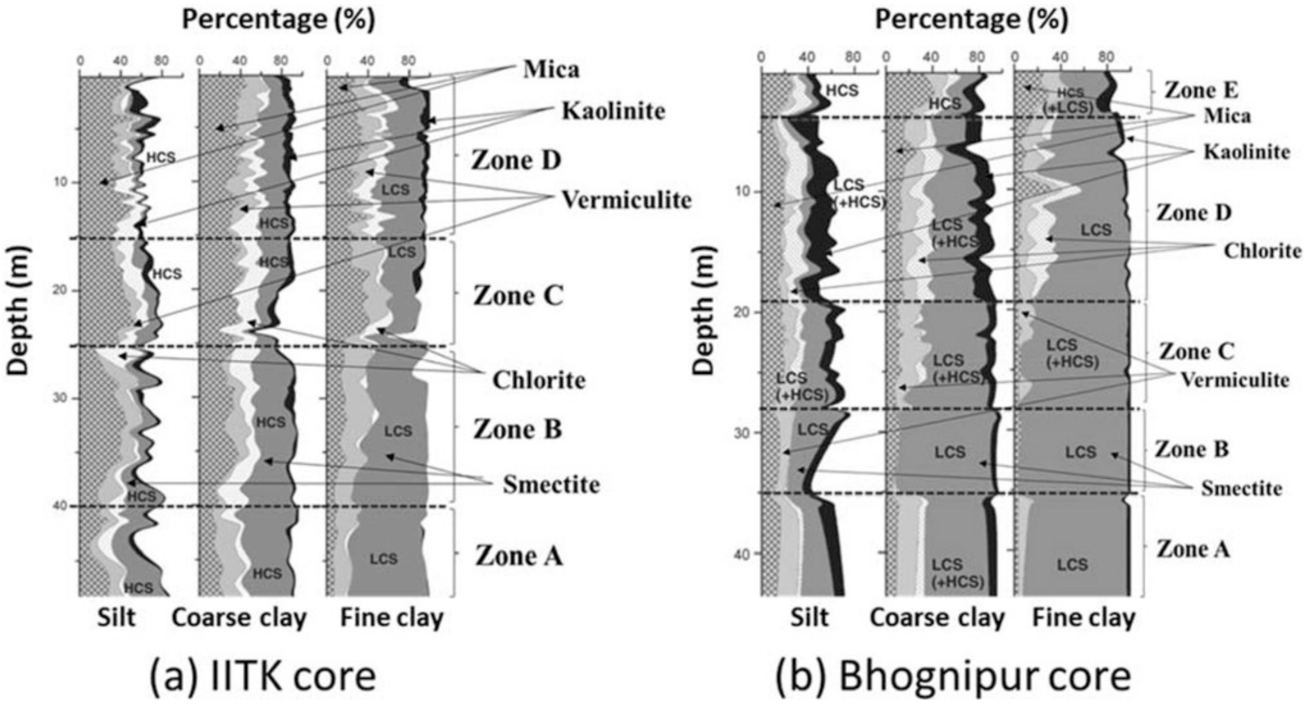

Fig. 6.3 Depth distribution of minerals in the silt, coarse clay and fine clay fraction of the cores collected from the **a** northern part of Ganga–Yamuna interfluve (IITK core), and **b** southern part of Ganga–Yamuna interfluve (Bhognipur core) (Adapted from Pal et al. 2012)

even though prevailing semi-arid climate cannot favour the formation of kaolin at the expense of smectite in slightly acid to moderately alkaline reaction. Similarly, the arid climate cannot yield the huge amount of smectite required for the formation of Vertisols. Earlier studies in southern peninsular India (Murali et al. 1978; Rengasamy et al. 1978) suggested that kaolinite was formed in an earlier geological period with more rainfall and great fluctuations in temperature, as evidenced by the presence of granitic tors all around such area (Pal and Deshpande 1987).

Two associated shrink-swell soils (red and grey coloured) occurring in a catena in the Hingoli district of Maharashtra were studied by Kolhe et al. (2011). The low hydraulic conductivity of red Vertisols was due to high Mg^{2+} and Na^{+} in the exchange complex. Mineralogical properties indicated that smectite was the dominant mineral in both the soils. The presence of kaolin in the grey Vertisols indicated the transformation of smectite to kaolin in the past humid climate. The absence of kaolin in red Vertisols indicated that the parent material (red bole) was not exposed to the earlier humid climate. They have been formed from the red boles mineral. The presence of palygorskite mineral with smectite in red shrink-swell soils and its absence in other associated soils in a catena indicated that this mineral cannot be considered as an index mineral for arid climate. The release of Mg^{2+} from palygorskite mineral disperses the clay and clogs the pores resulting in impeded drainage which adversely affect the crop production.

6.4.3 Smectite-Kaolinite Interstratification

Balbudhhe and Bhattacharyya (2009) studied the mineralogy and genesis of some representative rice-growing soils collected from four districts of eastern Vidarbha region of Maharashtra. They observed the dominance of smectites in the soil clays along with interstratified minerals of smectite-kaolinite (Sm/Kao) (Table 6.2). The interstratified Sm/Kao minerals developed from weathering of smectite minerals. They concluded that smectite present in the soils

Table 6.2 Semi-quantitative estimates of minerals present in total clay fraction (<2μm) of paddy-growing soils of Maharasthra, India (Balbuddhe and Bhattacharyya 2009)

Horizon	Depth (cm)	Minerals (%)[a]		
		Sm	Mica	Sm/Kao
Dighori soil (Bhandara)				
Ap	0–13	66 (72)[b]	8	26 (28)
Bw1	13–27	76 (82)	8	16 (18)
Bw2	27–53	77 (83)	8	15 (17)
Bss2	53–76	79 (85)	8	13 (15)
Bss3	76–105	81 (87)	7	12 (13)
Rajegaon soil (Gondia)				
Ap	0–10	49 (58)	15	36 (42)
Bt1	10–25	62 (72)	13	25 (28)
Bt2	25–55	56 (65)	14	30 (35)
Bt3	55–74	69 (76)	9	22 (24)
Bt4	74–107	74 (82)	10	16 (18)
Haldi soil (Chandrapur)				
Ap	0–14	80 (85)	6	14 (15)
Bw	14–46	83 (88)	6	11 (12)
Bsst	46–82	90 (94)	4	6 (6)
Bsst	82–114	82 (88)	7	11 (12)
Bsst	114–135	85 (90)	6	9 (10)
Kurul soil (Gadchiroli)				
Ap	0–12	88 (91)	4	8 (9)
Bw1	12–28	85 (90)	6	9 (10)
Bw2	28–50	81 (88)	8	11 (12)
Bw3	50–76	92 (95)	3	5 (5)
Bss1	76–101	89 (94)	6	5 (6)

[a] Sm: Smectite; Sm/Kao: Smectite-kaolinite interstratified minerals

[b] Parentheses indicate mineral content on mica-free basis

was developed as the first weathering product from plagioclase feldspars in earlier times under humid climate. The interstratification of Sm/Kao minerals was thought of as the result of post-depositional transformation. Smectite minerals prevailed due to poor drainage conditions, and only transformation was into Sm/Kao interstratified minerals.

Transformation of clay minerals in a soil chrono-association comprising five fluvial surfaces (QGH1 to QGH5) of the Indo-Gangetic Planis (IGP) between Ramganga and Rapti rivers demonstrated that the pedogenic Sm/Kao can be considered as a potential indicator for Holocene climatic changes from arid to humid conditions (Srivastava et al. 1998). The ages of QGH1 to QGH5 were <500 year before present (BP), >500 year BP, >2500 year BP, 8000 year BP and 13,500 year BP, respectively. During soil formation, two major regional climatic cycles were recorded. Relatively arid to semi-arid cycles between 10,000 and 6500 year BP and 4000 year BP till present was punctuated by a warm and humid climate. Biotite weathered to trioctahedral vermiculite and smectite in the soils during arid conditions that were unstable and transformed to Sm/Kao during the following warm and humid climate (7400–4150 year BP). When the humid climate terminated, vermiculite, smectite and Sm/Kao were preserved to the present. During the hot semi-arid climate that followed the humid climate, transformation of biotite into its weathering products like trioctahedral vermiculite and smectite did continue. Initiated by the formation of pedogenic carbonate, fine clay vermiculite and smectite translocated downward in the profile as Na-clay, to make soils calcareous and sodic (Pal et al. 1994, 2003). This pedogenetic process with time became an example of self-terminating process exhibiting their polygenetic features (Yaalon 1971).

6.4.4 Paleosols

Paleosols can act as important terrestrial archives containing information of the paleo-environment. But unscrambling the primeval pedogenic processes from paleosols might become difficult due to diagenetic alterations. Srivastava et al. (2013a) reported some important findings regarding the diagenetic alterations of the clay minerals of the oldest paleosols from the Himalayan foreland. Clay mineralogy of the paleosols revealed the presence of minerals like quartz, feldspar, vermiculite, kaolinite and mica in order of increasing abundance. Clay minerals in these paleosols underwent significant changes in terms of increased crystallinity, transformation and illitization due to burial diagenesis (around 7.5 km depth, and 140 °C temperature). Paleosols found in the fluvial sequences of Dagshai Formation near Koshaliya River, North West Himalaya were 0.5–1.5 m thick $B_k/B_{tk}/B_t/B_w/B_{ss}$ horizons, and showed prominence of pedogenic carbonates, rhizoliths and Fe-rich clay pedo features that belong to contemporary Inceptisols, Entisols, Vertisols and Alfisols (Srivastava et al. 2013b).

6.4.5 Layer Charge Characteristics of Smectitic Minerals in the Vertisols

The black soils of the Deccan Traps are rich in plagioclase feldspars which yield dioctahedral smectites as the first weathering product (Pal and Deshpande 1987; Pal et al. 1989; Bhattacharyya et al. 1993). Earlier review on the Vertisols of India indicates that black soils of India are dominated by beidillite-nontronite type of minerals (Ghosh and Kapoor 1982). Fine clay smectite, when subjected to the Greene-Kelly test (1953) involving heating the clay with lithium (Li) and subjecting to glycerol solvation, expands to about 1.8 nm and contracts to ~0.95 nm indicating this to be a mixture of beidillite/nontronite and montmorillonite in which the amount of the former is more than the latter (Pal and Deshpande 1987; Ray et al. 2003). Information on charge characteristics of Vertisols may be helpful to identify the smectite species in the mineralogical class instead of the group name, i.e., smectite. Another attempt (Bhople et al. 2011) has been made to locate the seat of charge of some Vertisol clays by determining the reduced CEC (CEC_R) of smectitic clays. Six benchmark Vertisols from Maharashtra namely, Linga, Loni, Asra, Paral, Kalwan and Nimone from Nagpur, Yavatmal, Amravati, Akola, Nashik and Ahmednagar districts, respectively, were chosen for the study. Fine clays were separated from the soils, and their original CECs (CEC_{UT}) were determined by exchange with neutral normal $MgCl_2$ followed by $CaCl_2$ and $BaCl_2$. Greene-Kelly test was performed by treating these clays with 3 *N* LiCl. The Li-clays were also treated with the above metal chlorides in the same order to get the reduced CECs. It was observed that the tetrahedral CEC decreased with increasing depth of soil for Linga, Asra, Kalwan and Nimone, whereas opposite trend was observed for Loni and Paral. The octahedral charge increased with depth for all except for Asra and Paral. The study indicated that the CEC determination appeared to be an accurate and less time-consuming approach to measure charge reduction. It can be used to locate the seat of charge and also to study the changes in the proportion of tetrahedral and octahedral charge during the pedogenic processes of soil formation.

6.4.6 Effect of Zeolite in Sand Fraction of Calcareous Vertisol

Formation of calcium carbonate ($CaCO_3$) has been reported to be a signature of dry (arid and semi-arid) climate (Pal et al. 2000; Raja et al. 2009). The increase in $CaCO_3$ content in soils is related to the development of sodicity as reflected by high exchangeable sodium percentage (ESP) (Balpande et al. 1996). The depth function of $CaCO_3$ and ESP (Pal et al. 1994, 2000) suggests that due to the formation of $CaCO_3$, sodicity develops initially in the subsoils. This subsoil sodicity impairs the hydraulic properties of soils. The initial impairment of the percolative moisture regime in the subsoils results in a soil where gains exceed losses. This self-terminating process (Yaalon 1983) subsequently leads to the development of sodic soils where ESP decreases with depth. Thus, the formation of pedogenic $CaCO_3$ is a basic process of initiation of chemical soil degradation (Pal et al. 2000, 2006). Against this background, it is experienced that some soils such as Nimone soils (Bhattacharyya et al. 2009**),** despite being calcareous and qualifying for Sodic Haplusterts, have not lost their productivity as evident from successful growing of agricultural crops. The reason for this has been attributed to zeolite in sand fraction of the soils. The sand fractions showed the presence of zeolites along with quartz and feldspar. Changes in phases of these zeolites on thermal treatments as indicated by shifting of 0.90 nm peak to 0.86 and 0.83 nm at 300 °C and its disappearance at 450 °C suggested that these zeolites belonged to Si-poor heulandites type (Bhattacharyya et al. 1993, 1997, 2006a; Pal et al. 2006). These base-rich zeolites have been reported to act as saviours for the Vertisols in the black soil region (Bhattacharyya et al. 1993; Pal et al. 2006). The presence of these zeolites helps in maintaining the productivity of these soils by two ways, viz. (i) supplying nutrient elements (Ca, Mg) in appropriate proportions and (ii) improving drainage for bringing right pedo-edaphic environment for crop growth. The presence of these zeolites is also responsible for the persistence of Alfisols (Bhattacharyya et al. 1999) and Mollisols in the Western Ghats and the Satpura (Bhattacharyya et al. 2006b). According to Bhattacharyya et al. (2009), mineralogical class of Soil Taxonomy should be based on pedo-edaphic datasets supporting resilience rather than any arbitrary nomenclature in view of contemporary natural chemical degradation process in terms of sequestration of inorganic C (as $CaCO_3$) and geogenic presence of natural modifiers (e.g. zeolites and gypsum).

6.5 Properties of Soil as Affected by Clay Minerals

6.5.1 Soil Physical Properties as Affected by Clay Minerals

Clay fraction controls many physical properties of soil which are agriculturally important. Pore size distribution of soils in relation to their clay mineralogy was studied for two Vertisols and two Alfisols of Andhra Pradesh by Nagarajarao and Prasadini (1991). Pore size distribution for the Vertisols was bimodal with peaks near aeration porosity and in the pore-size range of <0.01 µm. Montmorillonite with COLE (coefficient of linear expansion) value of >0.085 was the dominant mineral in Vertisols. The Alfisols showed a unimodal pore-size distribution with a peak in the aeration porosity range. The latter soils had lower clay contents with COLE values ranging from 0.008 to 0.027. Free-swell behaviour of bentonite clay was studied by Sridharan et al. (1992) after homoionizing it with different mono-, di- and tri-valent cations. Increase in cation valency led to decrease in free-swell index. For same valency, increase in hydrated size increased the free-swell index, and such effect was most prominent when bentonite was saturated with monovalent cations. The negative effect of cation valency on free-swell index could be due to its influence on the thickness of diffuse double layer, formation of quasi-crystals by divalent cation-saturated bentonites through the creation of outer-sphere complex between a pair of divalent cations and a pair of opposing siloxane ditrigonal cavities and aggregate formation by particles through hydrolysed Al or Fe ions in case of trivalent cation-saturated bentonites. Rengasamy (1999) studied the rheological properties of clays from Gondwana clay deposits of India. The clay dispersions in water showed non-Newtonian flow when subjected to different shearing stresses (0.0061–60 Pa) with different thixotropic critical stresses (1.5–13.5 Pa) and Bingham yield points (0.005–5.8 Pa) depending on the sample and its dispersion concentration. Creep responses of the dispersions were measured following the four element Burger's mechanical model.

6.5.2 Soil Chemical Properties as Affected by Clay Minerals

Adsorption of Zn at 25 °C and pH 5.6 on Na-kaolinite and Mg-kaolinite and kaolinitic soil clays from Alfisols was studied by Pal and Sastry (1985). They observed preferential Zn-adsorption throughout the range of surface coverage on both Na- and Mg-saturated clays. Very small amount of Zn (mole fraction 0.005) in solution was capable of replacing about 80% of Na from the surface. But at similar Zn: Mg ratio in solution, much less amount of Mg was exchanged. Muralidharudu and Raman (1985) studied the adsorption behaviour of Zn on homoionic soil clays saturated with Cu, Ca, Mg, Na and K at three temperature levels (30, 40 and 50 °C). The adsorption isotherms were well fitted to Freundlich model. Zinc adsorption per unit amount of clay increased in the order $Na < K < Ca < Mg < Cu$, and the amount adsorbed in each case was dependent on temperature and Zn concentration. Desorption studies in the same investigation showed that not entire amount of adsorbed Zn could be extracted into solution as some of the adsorbed Zn was fixed irreversibly in the system. Such fixation indicates 'ion trapping effect', which is likely to be more in clays where accessibility to interlayer spaces is more. Desorption decreased in the order Na-clay > K-clay > Ca-clay > Mg-clay > Cu-clay. Due to greater randomness and lower bond strength in Na-system, Zn adsorption was less, and desorption of adsorbed Zn was more. Zinc adsorption pattern on soil clays obtained from nine different soils (belonging Vertisols and Inceptisols) of Tamil Nadu was studied by Krishnaswamy et al. (1985). Their adsorption data conformed to both Langmuir and Freundlich adsorption equations. However, Langmuir gave better predictions of Zn adsorption capacities and adsorption energies. Among the nine soils, montmorillonite dominated soil clays showed higher values of adsorption maxima. Adsorptive capacities for Zn were positively correlated with clay CEC. Studies were carried out by Jain et al. (1985) on dielectric dispersion of adsorbed water on clay surfaces. Different clays showed different frequencies at which highest dielectric loss occurred. Kaolinite gave the maxima at around 500 Hz at low hydrations. Behaviour of illite in this regard was similar to that of kaolinite. Halloysite gave a peak at around 800 Hz and a second peak at around 5 kHz. Montmorillonite also gave the first peak at 800 Hz but the second peak at around 2 kHz. With increase in water content, the first peak initially became less prominent, then disappeared, while there was a shift in the second peak towards higher frequency. The authors concluded that the water molecules remain very closely attached to the clay surface at very low wetness and undergo Debye polar relaxation around 500 Hz frequency. Exchange equilibria on illite surfaces involving Na–Pb, Ca–Pb and Mg–Pb pairs at 30 and 60 °C were investigated at pH 5.5 using thermodynamic models (Khan and Khan 1985). Thermodynamic parameters (i.e. changes in enthalpy, entropy and standard free energy) showed that the preference of Pb for illite surface increased in the order Mg-illite < Ca-illite < Na-illite. The Mg–Pb exchange was found to be least ordered followed by Ca–Pb and Na–Pb exchanges.

Chatterjee et al. (2014) studied the fixation of P and K by non-colloidal (2–0.2 μm) clay-humus complex (NCH) and colloidal (<0.2 μm) clay-humus complex (CH) isolated from three contrasting soil orders, viz. Alfisol, Inceptisol and Vertisol. Alfisol showed the highest P fixation capacity (67.26% for NCH and 58.72% for CH), while Vertisol showed the highest K fixation capacity (37.94% for NCH and 32.57% for CH) for both the clay-humus complexes. They also observed that P fixation capacity of NCH was significantly and positively correlated with the contents of kaolinite, allophane, ferrihydrite, crystalline Al and Fe and poorly ordered Fe. For CH, P fixation capacity was positively related to the contents of kaolinite, ferrihydrite, crystalline Fe and poorly ordered Fe, but negatively related to organically bound Al. Potassium fixation capacity of NCH as well as CH showed significantly positive correlation with amorphous ferri-alumino silicate (AFAS) minerals. Potassium fixation in NCH was negatively correlated with the contents of kaolinite, ferrihydrite, crystalline Al and Fe and poorly ordered Fe.

6.6 Interaction of Clay Minerals with Humus

A range of amorphous aluminosilicates (AA) with different Si/Al molar ratios and their organic complexes with fulvic and humic acids were prepared and characterized by Basak and Ghosh (1996). The synthesized complexes were amorphous in nature mainly involving carboxylic groups in bonding between AA and organics. Allophane-humic acid complexes showed higher C contents than allophane-fulvic acid complexes. Organic C content was positively correlated with moisture in allophane-fulvic acid complexes and negatively correlated in allophane-humic acid complexes. Chattopadhyay et al. (2010) studied the interactions of soil fulvic acid (FA) and humic acid (HA) fractions with a siliceous allophane at different pH levels. Fixation of FA and HA by allophane decreased with increasing pH values due to the simultaneous development of negative charges on all of them. At any pH value, fixation of HA was much greater than that of FA due to less negative charges and hydrophilic nature of the former than the latter. Fixation of HA by allophane did not bring any considerable change in the X-ray diffraction pattern as the quantity of HA in the allophane-HA complex was not sufficient enough to bring such change. Response to infrared light of allophane-HA also remained almost same to that of allophane except in the 3500–3450 cm^{-1} zone, suggesting the interaction between HA and allophane to be weak in nature.

Ghosh and Mishra (1989) reviewed the research findings on clay-organic interactions. Das et al. (2013) studied the effect of humic acids separated from Alfisols, Entisols and Mollisols on the varying release of cations from olivine and tourmaline, rate of solubilisation, stability and characteristics of the residual products. Kinetics of solubilisation of the two minerals indicated a sequence of alternating dissolution and re-precipitation. They concluded that position of the cation in the crystal lattice and the stability of the cation-humic acid complex govern the release of the cation from the minerals. After the reactions with HAs, it was found that both the minerals, i.e., easily weatherable olivine and fairly resistant tourmaline have undergone significant changes. Infrared spectra indicated HA deposition on mineral surface which might have occurred after complexation. Das et al. (2014) also studied the interaction of HAs extracted from Alfisols, Entisols and Mollisols with biotite (phyllosilicate) and hornblende (inosilicate) and release of nutrients from them. Drastic changes in terms of reduction of Ca^{2+} and $Fe^{2+/3+}$ and augmentation of Si^{4+}, Al^{3+} and Mg^{2+} were observed in hornblende, while biotite showed minimal alteration. Prominent XRD bands of hornblende either attenuated or disappeared in the reacted residues with the formation of several new crystalline phases. Biotite, on the contrary, showed slight alteration in the crystalline phases. Infrared spectra revealed that HA was deposited on the surface of both the minerals, with more prominent deposition being observed on hornblende.

6.7 Interaction of Clay Minerals with Pollutants

Pesticides used in intensive agricultural practices to control insect pests, weeds, diseases, etc., may sometimes persist in the soil too long to cause damage to soil health. Soil components like clay minerals can alter their bioactivity by specific interactions. The metal ions present in clay colloids have the ability to influence adsorption and degradation of such compounds. However, the extent of such activity depends on the clay minerals present in the soil where the pesticides have been applied. In this regard, Agnihotri and Raman (1982) studied the adsorption of metribuzin, a herbicide, on homoionic chlorite dominant clay at 5 and 35 °C temperatures. Freundlich equation well described the adsorption isotherms. Extent of adsorption followed the order: Ca-clay < Zn-clay < Na-clay < Cu-clay < Al-clay. In all the cases, adsorption was more at 5 °C temperature than that at 35 °C temperature.

Carbofuran and bendiocarb are broad spectrum systemic insecticides. Garg and Agnihotri (1984) carried out a study to observe the adsorption of carbofuran and bendiocarb on soils of varying mineralogy (alluvial, red, black and forest soil) and reference clay minerals, namely kaolinite, vermiculite and bentonite at three different pH (5.0, 7.0, 9.0) levels. Freundlich equation best described the adsorption data. Amount of adsorption increased in the order: kaolinite < vermiculite < bentonite and also increased with decrease in pH. Shifts in bands at 2920, 1745 and 1225 cm^{-1} of IR spectra due to adsorption of insecticides indicated the involvement of $–CH_2$, –C=O and –C–O–C– groups. Desorption study showed that not more than 43% of carbofuran and 23% of bendiocarb got desorbed indicating the irreversible nature of the sorption reactions of insecticides on soil solid surfaces.

Raman and Rao (1984) studied the adsorption behaviour of metoxuron, a herbicide, on homoionic montmorillonitic clays. The charge and the polarizing power of the saturating cations mainly governed the extent of metoxuron adsorption on the clay surface. Adsorption was maximum on H-clay, Fe-clay and Al-clay followed by Ni-clay, Zn-clay, Cu-clay, Mg-clay, Ca-clay and Ba-clay. Clays saturated with Na, K or NH_4 showed the least adsorption. Adsorption maxima showed a positive correlation with crystalline ionic potential indicating ionic potential to be the main driver in binding of metoxuron to metal clays. Adsorption maxima values also indicated that mostly the edges and less likely the interlayers were involved in adsorbing metoxuron.

Sharma et al. (1993a) studied the adsorption of Topsin-M, a systemic fungicide belonging to thiophanate group on Na- and H/Al-saturated illites and montmorillonites at 20 and 40 °C temperatures. Adsorption of the fungicide, at 20 and 40 °C temperatures, followed the order: Na-illite < H/Al-illite < Na-montmorillonite < H/Al-montmorillonite. Increase in temperature led to decrease in adsorption of Topsin-M. They concluded the adsorption to be more of physical than chemical in nature. Thermodynamic parameters studied by Sharma et al. (1993b) for Topsin-M adsorption on Na- and H/Al- saturated illite and montmorillonite showed that in all the cases thermodynamic equilibrium constants (ln K°) were more than one, which indicate high affinity of Topsin-M (Thiophanate-methyl) for the clay surfaces. This affinity for adsorption decreased with increase in temperature. The $\Delta G°$ values were negative confirming that the reactions were spontaneous, and the spontaneity decreased with rising temperature. Narayanan et al. (2014) observed the effect of clay on leaching of three pesticides, viz. chlorpyriphos, chlorothalonil and pendimethalin in an Inceptisol. Their study showed that in normal soil, leachates contained around 2% pesticides, but in the same soil after partial removal of clay fraction, the leachates contained as high as 5–25% pesticides.

Chloramine-T (sodium N-chloro paratoluene sulphonamide) is a very common oxidizing agent used in analytical chemistry. Jai Prakash and Jaya Kumar (1984) studied the adsorption behaviour of chloramine-T on Zn-montmorillonite at two different temperatures (5 and 40 °C). Freundlich isotherm showed better fit to adsorption data than Langmuir isotherm. The heat of adsorption (334 cal mol^{-1}) indicated that forces like van der Waals or H-bonding between the oxygen on the mineral surface and the amino group of the adsorbate might have caused the adsorption to occur.

Heavy metals in high concentrations have toxic effects on agriculture, ecosystem and human health and pose very serious environmental problems. Kumararaja et al. (2014) evaluated the effectiveness of a bentonite clay in removing two heavy metals (Zn and Cu) from aqueous systems and their subsequent immobilization. They found maximum adsorption of Zn at pH 7 and that of Cu at pH 6 (Fig. 6.4).

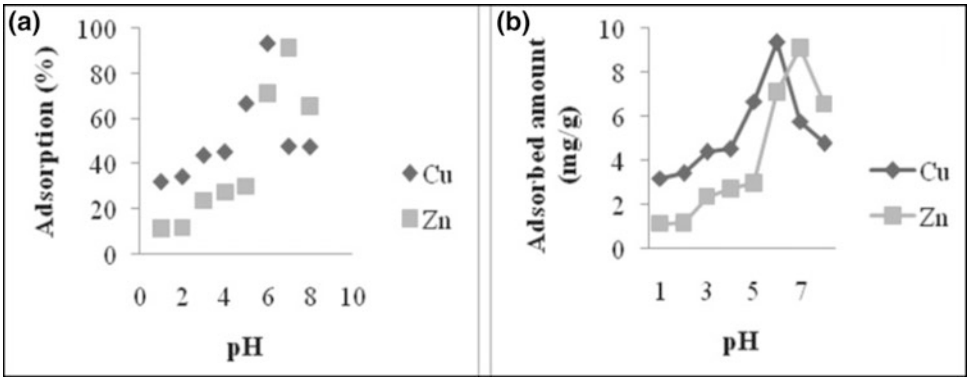

Fig. 6.4 Effect of pH on **a** removal (%) and **b** adsorption capacity (mg/g) of bentonite clay for Zn and Cu (Kumararaja et al. 2014)

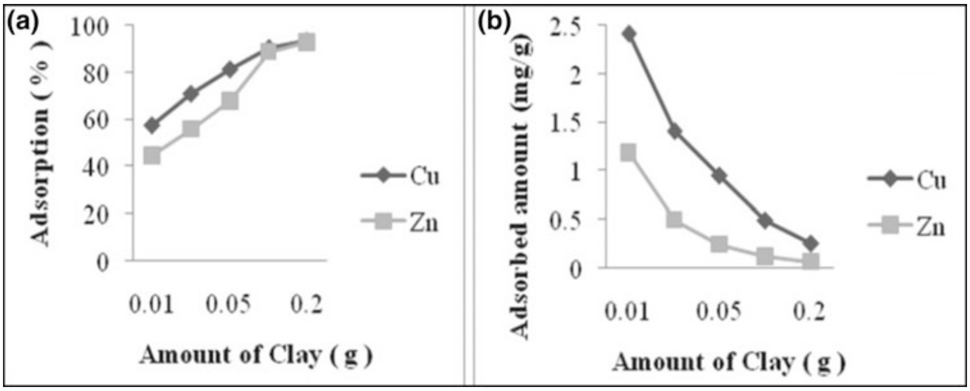

Fig. 6.5 Effect of amount of adsorbent on **a** removal (%) and **b** amount of metal (Zn and Cu) adsorbed per unit amount of adsorbent (Kumararaja et al. 2014)

Proportion of heavy metals removed from aqueous system increased with increase in the amount of adsorbent and decreased with increase in the initial concentration of the heavy metals in the aqueous system (Fig. 6.5). They concluded that bentonite could be useful in removing heavy metals from water through adsorption.

Radionuclides entering into soils and water sources may put at risk the ecosystem stability and become a serious threat to animal and human health. Radio-caesium, the most important artificial radionuclide, has found its entry point to the terrestrial environment for many years through the testing of nuclear weapons, accidental leakage from nuclear facilities, and authorized expulsion of nuclear waste. Agricultural product grown in such contaminated soils acts as the primary route for this radionuclide to enter into the food chain. Uptake of such radionuclide by plants depends on its retention in soil by interactions with the solid phase. In this context, Sandeep and Manjaiah (2009) studied the sorption-desorption behaviour of radio-caesium in soils and clay minerals (kaolinite, halloysite, attapulgite, nontronite, vermiculite, mica and illite) under the influence of oxalate and sodium tetraphenylboron. They found that more than 90% of radio-caesium (^{134}Cs) got adsorbed by soils and clays even in the presence of competing solutions (e.g. sodium oxalate). Halloysite and attapulgite showed the minimum adsorption (96.7%) followed by kaolinite (97.1%), vermiculite (97.2%), illite (98.0%), mica (98.7%), and highest adsorption was shown by nontronite (99.4%). Red and laterite soils showed maximum desorption; while among the clays, maximum desorption was observed for attapulgite. Sorption-desorption studies of ^{134}Cs on clay fractions and clay-sized aggregates separated from seven important soil orders found in India showed that sorption of ^{134}Cs was lesser in clay-sized aggregates with the lowest values being observed in Ultisols and Aridisols (Fig. 6.6) (Chari and Manjaiah 2010). Sorption significantly increased when organic matter was removed from the aggregates. On the contrary, ^{134}Cs sorption drastically reduced when sesquioxides were removed from clay samples. Sorption was more in smectite and mica than kaolinite. In waste mica, sorption increased by around 1.2 times with decrease in size of the particles. Desorption study showed that 1.2–7.3% of the sorbed ^{134}Cs could be extracted and the effectiveness of the extractants in this regard was in the order water < $CaCl_2$ < KCl < NH_4Cl (Fig. 6.7).

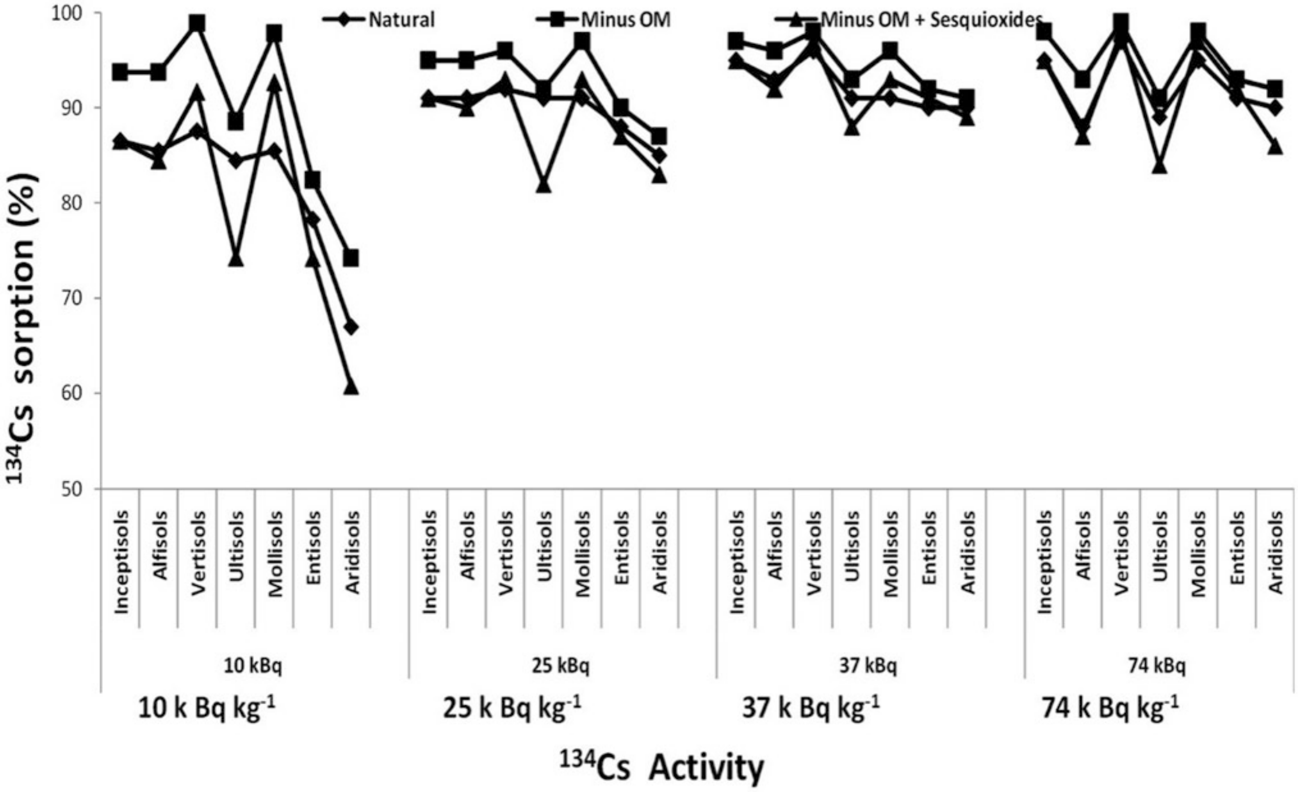

Fig. 6.6 ^{134}Cs sorption (%) on clay aggregates as influenced by its activity levels (Chari and Manjaiah 2010)

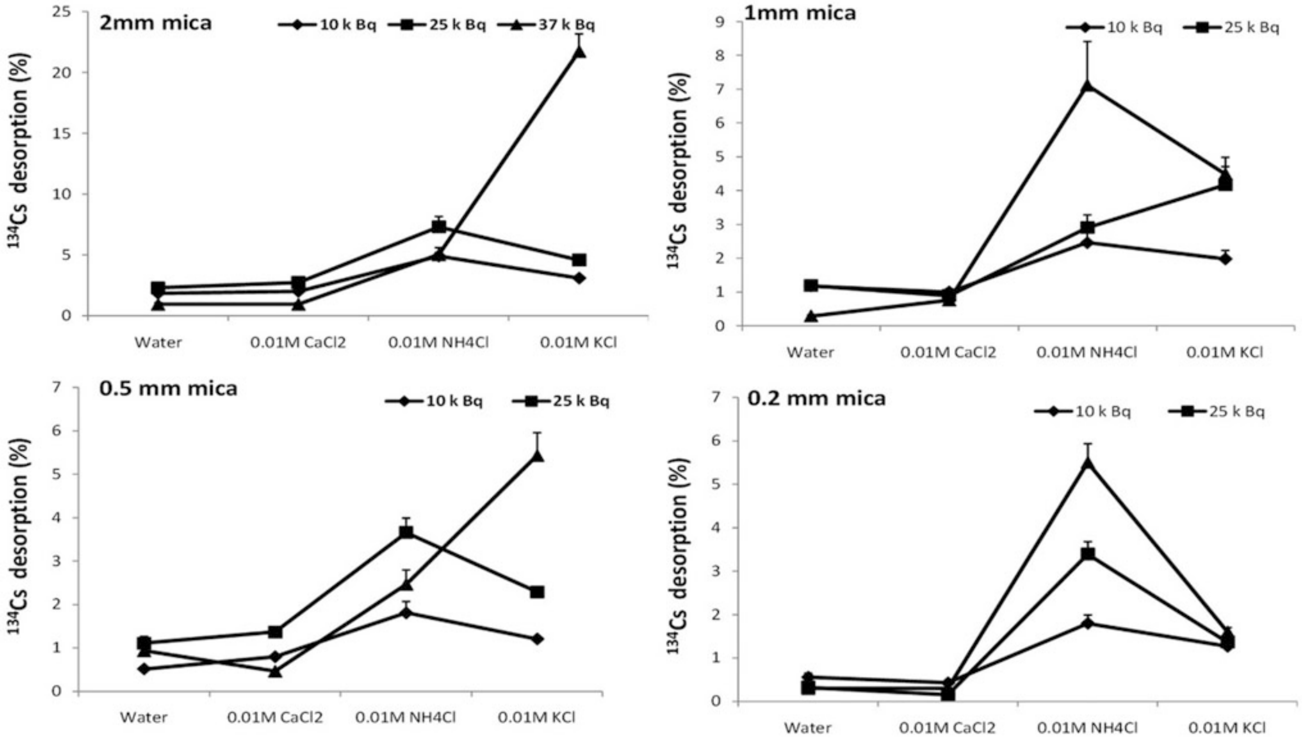

Fig. 6.7 ^{134}Cs desorption (%) from waste mica as influenced by extractants (Chari and Manjaiah 2010)

Table 6.3 Characteristics of resolved peaks obtained from deconvolution and curve fitting of XRD profile of soil clay (<0.02 µm) in the range of 4–11° 2θ (Datta 1996)

Peak no.	d-spacing (Å)	Mineral	Width		Mean thickness of crystallites (no. of units)	Strain (%)	Peak area (% of total)
			Gaussian	Cauchy			
			2θ				
Udic Ustochrept							
1	9.96	Mica	0.12	0.34	260	1.3	12
2	10.3	Mica-chlorite	0.66	1.54	–	–	53
3	13.9	Chlorite	0.76	1.68	53	11.9	35
Vertic Ustochrept							
1	15.1	Smectite	0.53	1.39	63	9.0	78
2	12.1	Mica-smectite	1.1	2.68	–	–	17
3	10.6	Mica-smectite	0.69	0.87	–	–	5
Typic Halpustalf							
1	14.6	Chlorite	0.487	1.156	77	8.0	22
2	11.66	Chlorite-mica	0.649	2.12	–	–	47
3	9.93	Mica	0.362	0.866	102	4.0	31

6.8 Advanced Studies on Clay Mineral Structure, Size and Crystallinity

Effect of heating on absorption of infrared light by layer silicates was studied in clay fractions separated from one kaolinitic and four illitic soils (Banerjee 1992). It was observed that the IR absorption bands specific to OH groups of layer silicate minerals were present when the samples were kept at room temperature. The same bands eliminated when the clay samples were heated to 1050 °C. However, the heated samples showed broad bands at 3420 and 1620 cm^{-1}. Origin of such bands could be attributed to the development of structural defects at high temperature and residual water after rehydration.

By curve-fitting and deconvolution of XRD profile, Datta (1996) characterised some micaceous minerals present in soils for size and strain of crystallites. For this purpose, oriented samples of fine clay fraction (<0.2 µm), isolated from Udic Ustochrepts (57% illite), Vertic Ustochrepts (49% smectite) and Typic Haplustalfs (81% kaolinite), were scanned by X-ray diffractometer (Table 6.3). The effect of instrumental broadening was eliminated from the observed X-ray peak by an iterative deconvolution programme followed by Lorentz-Polarization (LP) factor correction. Then the cluster of peaks was resolved into individual peaks by fitting the LP corrected digital data to a pseudo-Voigt function by a non-linear regression programme. This programme optimized the parameters, e.g., true position, intensity, Cauchy and Gaussian components of each of the peaks present in the cluster. Strain and particle size were then determined from Gaussian and Cauchy components, respectively. The study showed that micaceous mineral found in the Udic Ustochrepts was bigger and more crystalline than those present in Vertic Ustochrepts and Typic Haplustalfs.

6.9 Conclusions

Soil mineralogy with special emphasis of clays and clay minerals plays vital role in the study of soil resource. Some of the clay minerals like kaolinite, montmorillonite, vermiculite, etc., have been found to have the ability to adsorb different pesticide molecules and reduce their leaching into the groundwater. Sometimes, the bioactivity of such pesticide molecules is altered upon interaction with clay minerals. Such properties of clay minerals are very important for the maintenance of soil health and groundwater quality.

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