

**MINERALOGY AND SURFACE PROPERTIES OF THE CLAY FRACTION
AFFECTING SOIL BEHAVIOUR AND MANAGEMENT**

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Abstract

The mineral composition of the clay fraction is discussed in terms of crystal structure and of chemical and physical properties related to mineralogy. The main transformation processes affecting the clay fraction and the conditions in which they occur are briefly described. Examples are given of relations between landscape position, dominant transformation process and clay mineralogy. Differences between surfaces of clays and their bulk composition may arise naturally, as external conditions change, and by the action of man. Although it is generally impractical to attempt changes in composition of the clay fraction, some changes in surface properties are feasible. These may mask or alleviate undesirable characteristics of the clay fraction as a whole.

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Changing the fertility of a soil is a relatively simple, although temporary, measure. It is more difficult to change the physical or hydrological characteristics of a soil, although cultivation measures, drainage and irrigation or mulching can bring about desired changes for a season or a longer period.

The clay mineral composition of a soil generally cannot be changed by economic means within a human lifetime. The user of the land has to live with the mineralogy of the clay fraction.

In rare cases, rapid changes may occur in the clay fraction of soils. For example, there are indications that halloysite, a crystalline clay mineral, may be formed in an amorphous clay fraction within a few years once the soil dries out periodically. Such instances can be found in young volcanic materials when an original rainforest is cut and replaced by arable crops.

In 1934, Edel^lman hypothesized that the clay fraction of soils could consist of mixed gels containing Si, Al and bases, as well as crystalline layer silicates of different kinds, and that these could be formed from weathering products of the primary minerals in the coarser fractions. He also postulated that the crystalline clays could consist of complicated mixed crystals: both in the sense of mixed layer structures and in the sense of solid solutions containing a range of major and trace constituents.

This balanced and modern view was in contrast to others, who neglected

structure considerations or contents of bases, and considered the clay fraction to consist of an inorganic, colloidal, hypothetical soil acid (termed, e.g., pyrophyllic acid because of its similarity in composition to pyrophyllite).

We shall need to consider the crystalline nature of the bulk of the clay fraction in many soils, the presence of amorphous or x-ray amorphous material which may determine the surface properties of the clay fractions, and the important and rapid changes that may occur in the surface of the clay fraction, even while the bulk of the material may remain substantially unchanged in composition or structure.

The references in this paper include several chapters of a book which I still consider to be the best single source of information on the clay fraction of soils, also for non-clay mineralogists: Dixon and Weed (eds), 1977.

MINERAL COMPOSITION OF THE CLAY FRACTION

The properties of a soil are determined to a large extent by the proportion and the nature of the clay fraction. In most soils, this consists of

- layer silicates (clay minerals in the strict sense);
- other crystalline minerals such as quartz, anatase, or palygorskite (a magnesium-aluminium silicate with a fibrous structure), which will not be discussed here;
- iron and, in some cases, aluminium oxides and hydroxides, which may be crystalline or amorphous;
- amorphous or paracrystalline aluminosilicates (allophane, imogolite);
- organic compounds associated with the mineral part of the clay fractions.

Some properties of the mineral materials are summarized in Table 1 and further discussed below.

Most soils in plains contain an assemblage of clay minerals, while upland soils tend to have a simpler clay mineralogy. In both cases, one or a few clay minerals may dominate the soil properties.

For practical purposes, two broad groups of clay minerals may be distinguished: a group with permanent charge, which have a moderate or high cation exchange capacity (cec) at all pH values of interest, and a group with pH-dependent charge.

Clay minerals with permanent charge

The clay minerals with permanent charge have layers consisting of two tetrahedral sheets enclosing an octahedral sheet: mainly silica and mainly aluminium or magnesium oxide, respectively. Substitution of Al or Fe(III) for Si in the tetrahedral sheets, or of Mg, K or Fe(II) for Al in the octahedral sheet causes the permanent charge of the mineral. The swelling clay minerals or smectites such as montmorillonite, beidellite, nontronite are examples of this group.

The exchangeable cations that compensate the permanent charge are electrostatically bound to the clay surfaces; part of them, aluminium in particular, closely attached to the surface, the remainder in a diffuse layer, rather like the atmosphere over the earth's surface. In the nearby parts of this layer there are very few anions, because of electrostatic repulsion, and the water molecules near to the clay surface are firmly oriented by the electric field: not free, like in water. The diffuse layer is thin where the exchangeable cations are largely trivalent (Al) and divalent (Ca, Mg), and where the soil solution is concentrated. With increasing dilution, or an increasing proportion of monovalent cations (Na), the diffuse layer becomes thicker.

Such clays can contain much water in their diffuse layers that is unavailable to plants. In the smectite clay soils of the Sudan Gezira, for example, moisture depletion by plants stops at about 25 mass per cent, while soil saturation is at about 36 mass per cent (Farbrother, 1970). While water can be transported through the diffuse layers, albeit slowly, salts cannot because of the exclusion of anions from them (Smiles and Bond, 1984). This causes a low efficiency of salt removal from saline heavy clay soils: salt concentrations in the drainage water are lower than in the soil solution.

This is not the only reason for relatively low efficiencies of salt removal from clays with a high cation exchange capacity. Most swelling clay soils are structured, having peds surrounded by cracks owing to shrinkage ; many also have tubular pores that are due to biotic activity. As Bouma and co-workers have shown in several studies (references in Bouma, 1984), part of the irrigation water applied on a structured clayey soil flows through the large voids and is drained without removing more than a small fraction of the salt within the peds: a process called short-circuiting. If soluble plant nutrients are applied to the soil surface in such a system, part of these would also be

removed below the rooting zone by rain or irrigation water short-circuited through large voids, because of insufficient contact with the cation exchange sites within the structural elements.

The salt-sieving effect can be minimized, but not entirely avoided, by keeping the salt concentration high for as long as possible and increasing the proportion of di- and trivalent cations. Short-circuiting can be minimized or eliminated by lowering the rates of water movement through the soil to avoid saturation, e.g. by low rates of irrigation water application or by puddling the surface horizon.

Swelling clay soils may become virtually impervious by water saturation, for example under wetland rice, or by excessive or frequent irrigation. Shrinkage by drying generally restores the structure of the surface horizon and the hydraulic conductivity of the subsoil horizons through the formation of an intersecting system of cracks. This is useful for dryland crops after wetland rice, for example.

In soils with high shrink-swell ratios, bulk density is probably not limiting for root penetration (Jones, 1983), in contrast to other soils.

On slopes in water-saturated conditions, soils containing mainly smectite are subject to slow creep of the surface material or sudden deep slumping along a rotational plane (Istok and Harward, 1982).

The swelling clay minerals have a moderate proportion of substituted atoms, hence a relatively low charge density. For that reason, the exchangeable cations are bound only moderately strongly, spread out in a diffuse layer. Each layer of the clay structure contributes to the cation exchange capacity and to the swelling characteristics.

Other clay minerals with a similar structure have much higher proportions of substitution, hence a high charge density: illite and vermiculite. These bind certain cations with enough energy to fix them between adjacent layers in non-exchangeable form. Particularly ions such as K, which fit neatly in holes in the clay structure, serve to produce a rigid stack of clay layers. Only the outer surfaces and, to a varying extent, imperfectly fitting layers within the stacked structure, then contribute to cation exchange, and these clay minerals swell and shrink much less than the smectites. On the one hand, these clay minerals contain much K within their structure, and this becomes available to plants, but slowly, during weathering. On the other hand, parts

of the clay structure that are depleted of K can very readily fix fertilizer K (Douglas, 1977, p. 285-287; Borchardt, 1977, p.314) when this is present in temporarily high concentration. Since the ammonium ion is physically very similar to potassium, NH_4^+ can also be fixed by vermiculite or K-depleted illite (IRRI, 1983), but somewhat less strongly.

One of the swelling clay minerals, beidellite, has a structure in which NH_4^+ fits particularly well. Soils containing beidellite fix ammonium very strongly, as well as K (Bajwa, 1981a).

Clay minerals with pH-dependent charge

The clay minerals with variable charge have layers consisting of alternating tetrahedral silica and octahedral aluminium hydroxide sheets, with very little substitution charge. The main examples are kaolinite and halloysite. Kaolinite normally occurs as hexagon-shaped or rounded flakes, of the order of 1 μm in diameter, much coarser than the swelling clay minerals. Halloysite occurs in two variants: a hydrated form containing water layers between the clay layers and a dehydrated form, similar to, but less well ordered than kaolinite. Halloysite often occurs as curved or rolled plates (tubular) or as globular aggregates, much finer than most kaolinites.

The aluminium at the edge of the sheets is positively charged, particularly at low pH, which produces a small anion exchange capacity. Whereas ions such as chloride or nitrate are in fact exchangeable on such sites, phosphate and silica are bound tightly, and remain fixed (Muljadi et al, 1966; summary in Dixon 1977, p. 388). Kaolinites generally have a relatively coarse particle size, and in that case the amount of fixation is small. Fine-grained kaolinites as well as halloysites, which are extremely fine-grained with large edge areas, can fix large amounts of applied phosphate (Bajwa, 1981b).

These clay minerals have a very low cec, increasing with pH by dissociation of OH groups. They show virtually no swelling or shrinkage with changes in water content. Soils dominated by kaolinite or halloysite generally have no or only weak ped structure. For such soils, Jones (1983) estimates that root penetration is impeded above a critical bulk density, $(1.2 + 0.005 \times \text{sand } \%)$

Soils on steep slopes having a clay fraction with small water holding capacity, for example mainly kaolinite or dehydrated halloysite, are not subject to creep or slumping, but may form debris avalanches in very wet conditions where bedding planes of the rock run parallel to the slope (Istok

and Harward, 1982).

Once soils dominated by kaolinite or halloysite have become dense by land clearing activities, by rain impact, or by wheel or bullock traffic or plough pressure during cultivation, they do not regain their structure and hydraulic conductivity by wetting and drying like the swelling clay soils, but need to be restored by biological or mechanical means. This can be done by stimulation of worm activity through mulching. Initial ripping or cultivator treatment may be useful, but only if the soil is dry or moist. The same problem occurs where such soils are puddled for a wetland crop and subsequently used for a dryland crop. Procedures for safe management of such soils are given, e.g., by Vierhout (1983).

Aluminium-interlayered materials

In certain soils containing clay minerals with permanent charge, the interlayer spaces of these clay minerals are blocked by sheets of partly neutralized aluminium ions. These sheets, incomplete and generally poorly ordered, consist of ring structures such as $Al_6(OH)_{15}^{3+}$. They are not exchangeable, neutralise a considerable part of the cec, and restrict the swelling that can take place. Fairly complete aluminium interlayers thus convert clays with permanent charge into materials similar to kaolinite.

Even moderate proportions of aluminium interlayering have a great effect on stability of clays against dispersion, as experimentally verified by Muranyi and Bruggenwert (1984). At low salt concentrations, an illite clay soil material dispersed and collapsed into a virtually impermeable mass at exchangeable sodium percentages (ESP) about 30 and above, whereas the partly aluminium-interlayered material remained permeable at all ESP values tested, up to 80 percent.

This may be relevant for the reclamation of sodic, or saline-sodic soils. Acid formed after application of sulfur or of finely ground pyrite as in parts of India, or waste acid from chemical industries, as used locally in the U.S.S.R, presumably dissolve some aluminium from clay minerals besides Ca from lime that may be present. This would produce aluminium interlayers besides dissolved calcium sulfate, both aiding reclamation.

Oxides and hydroxides of iron(III) and aluminium

Soils containing low-activity clays (clays fractions with a low cec)

often contain gibbsite ($\text{Al}(\text{OH})_3$) besides kaolinite, generally as discrete clay-sized particles. This material aggravates the management problems of such soils, because its cec as well as moisture-holding capacity are essentially zero, and because applied phosphate is fixed more severely by gibbsite than by kaolinite.

Iron(III) oxides, too, may occur in the clay fraction as discrete, crystalline particles of goethite or hematite. These two generally have a relatively low specific surface and have similar properties as gibbsite, at least in well drained soils.

Iron oxides or hydroxides can also form generally discontinuous coatings on kaolinite and other clay minerals. These are often amorphous, have a very high specific surface, and drastically modify the charge characteristics and the physical properties of such soils. The cation exchange capacity is very low. Phosphate fixation is severe and remains severe except after very large phosphate applications. The structure stability is much higher than that of kaolinitic soils with low proportions of iron oxides: infiltration rates remain high even after rainfall impact and the pores collapse less readily by traffic.

In surface soils with high organic matter contents, the association of organic matter with the iron oxides counteracts all these effects to some extent. Wetland conditions, too, modify the effects of the finely distributed iron(III) hydroxides. Reduction of iron(III) phosphates increases phosphate availability; reduction of Fe(III) oxides to Fe(II) increases cec directly as well as by the associated rise in pH.

Amorphous aluminosilicates

Amorphous aluminosilicates and related materials which only have short-range order include allophane and imogolite. These occur in many young volcanic soils. Such soils have very high moisture retention and phosphate fixation and a low to very high pH-dependent cec. They may contain very high proportions of organic matter, presumably protected against rapid microbial decomposition by the association with large amounts of aluminium.

These soils are quite stable against rain impact and not erodible, but may fail under load. Failure may occur in the form of landslides, slumps or creep (Warkentin and Maeda, 1980). Soils containing amorphous clay constituents and hydrated halloysite may turn liquid, and slow-moving earthflow over considerable depth may occur frequently, even where overall

slopes are not very steep (Istok and Harward, 1982).

All the types of failure mentioned for soils with different clay mineralogies occur in water-saturated condition. Prevention in a landscape with wetland terraces would have to depend on drainage at the bottom of the terrace walls and, where possible, on careful construction of the terraces with the most slowly permeable material in the surface layer. These techniques have been raised to the level of a fine art by the Ifugaos of central Luzon, Philippines (Moormann and van Breemen, 1978, p. 89-90; van Breemen et al. 1970, p. 39-73).

ORIGINS OF THE CLAY FRACTION; TRANSFORMATION PROCESSES

The clay fraction in soils may be transported and deposited, together with other fractions of the sediment; it may be inherited from a sedimentary rock that has physically weathered; or it may have been formed by weathering of minerals in coarser fractions, or transformed from other clay minerals.

On young land surfaces, such as recent alluvial plains or slopes with a moderate or high rate of erosion, the nature of the clay fraction is largely determined by the original material. Since many sediments have a rather wide source area, their clay fractions often are a mixture of, e.g., illite, montmorillonite or vermiculite with or without some aluminium interlayering, kaolinite and some clay-sized quartz. Such mixtures tend to be rather constant within an alluvial plain but may vary from one river plain or estuary to another.

On older land surfaces, for example on river or coastal terraces or in upland areas with little erosion, weathering and clay transformation become more important. A few major clay transformation processes, acting on a variety of original materials, can explain the different clay mineralogies that may occur. These processes, discussed at some length in Brinkman (1982), are summarized below. They are the following five, in order of decreasing areal importance.

- Hydrolysis by water containing carbon dioxide, which removes silica as well as basic cations.
- Cheluviation, which dissolves and removes especially aluminium and iron by chelating organic acids.

- Ferrolysis, a cyclic process of clay transformation and dissolution under the influence of alternating reduction and oxidation of iron, which lowers the cec by aluminium interlayering.
- Dissolution by strong mineral acids, which attacks all clay minerals, producing acid aluminium salts and amorphous silica.
- Clay transformation under neutral to strongly alkaline conditions (reverse weathering), which may give rise to minerals such as montmorillonite, or in extreme cases palygorskite or analcime.

Hydrolysis by water containing carbon dioxide

Hydrolysis by water containing CO_2 , also called desilication, sometimes referred to as "weathering" without further specification, is a dominant process of clay formation and transformation particularly in the humid tropics, but also in part of the temperate zone.

Water in equilibrium with atmospheric CO_2 has a pH of about 5.6, the same as uncontaminated rain water. When excess rain water passes through a soil, clay minerals begin to dissolve congruently (proportionately) until the solubility product of gibbsite, $\text{Al}(\text{OH})_3$, is reached. This happens already at an Al concentration of the order of 10^{-9} mol/l at pH values about 5.5 to 6. From then on, gibbsite is precipitated while clay minerals continue to dissolve and silica is removed by the percolating water. Thus, gibbsite is formed in, e.g., kaolinitic soils under perhumid conditions.

Where leaching is less rapid and where the clay fraction contains minerals such as montmorillonite or illite, which contain a high proportion of silica as well as basic cations, continued dissolution causes the silica concentration to rise further, above about 10^{-4} mol/l. Then, kaolinite is stable over gibbsite, so kaolinite may be formed from, for example, montmorillonite or feldspars under humid conditions.

In both these cases, any iron that is released from the mineral structure is precipitated as hydroxide or as goethite (FeOOH) because of its extremely low solubility.

Where concentrations of Mg or other structural cations are relatively high during weathering, montmorillonite or vermiculite may be transformed into their aluminium-interlayered equivalents, because these are stable over kaolinite and gibbsite under these conditions. Even in cases where kaolinite is stable over the aluminium-interlayered material, the latter may still be formed as an intermediate step in the transformation sequence.

The stability relationships referred to in this section are based on thermodynamics, but can be visualized most simply in terms of solubility products that determine whether a given compound dissolves or is precipitated.

Hydrolysis of clay minerals or of feldspars or other weatherable minerals in coarser fractions is a slow process, in which silica is removed at rates of about 1 to 10 mg/l, and basic cations at similar or lower rates.

Where potassium concentrations in solution are kept very low by plant uptake, dissolution of K from illite may proceed faster than desilication of the material. Then, illite may be transformed into K-depleted (swelling) illite, and with further minor changes into vermiculite or a swelling clay mineral similar to beidellite. These, in turn, would be subject to the slower transformations discussed above.

Decomposition by strong acids

When pyrite clays, occurring in many mangrove areas, are oxidized by drainage, sulfuric acid is formed by oxidation of the pyrite. This rapidly dissolves clay minerals, at pH values between 2.5 and 3.5, until the silica concentration is about 2×10^{-3} mol/l (about 120 mg/l). Then, amorphous silica is precipitated.

If Mg and K concentrations are high enough, for example in saline conditions, montmorillonite and illite may be stable with respect to kaolinite. Then, the direction of clay transformation is away from kaolinite, in contrast to hydrolysis.

Dissolution by strong acids gives rise to aluminium concentrations ranging from 1 to some hundreds of mg/l, several orders of magnitude higher than in hydrolysis by water with CO_2 , and to silica concentrations of about 100 mg/l, about 10 times higher (van Breemen, 1976). The process can therefore proceed much faster than hydrolysis if the reaction products are removed, e.g., in drainage water.

Reaction products that are not removed may form amorphous silica and aluminium interlayers in swelling clay minerals once the pH has risen again to about 5 or higher.

Cheluviation

During cheluviation, organic acids specifically dissolve aluminium and iron, and remove them in chelated form. The direction of clay transformation is

similar to that during dissolution by strong acids.

Cheluviation occurs extensively in humid climates with a cold season, but only locally in very poor, sandy materials with poor drainage in the humid tropics. It is not discussed here because it is of negligible importance in wetland or dryland rice areas.

Ferrolysis

Clay decomposition and transformation by ferrolysis requires two alternating sets of circumstances. During water-saturated conditions with some leaching, the soil is reduced and the pH rises slowly by the conversion of $\text{Fe}(\text{OH})_3$ into Fe^{2+} , which becomes exchangeable as well as soluble. Part of the exchangeable basic cations are removed by leaching. Water saturation alternates with drying and oxygen entry. Then, exchangeable Fe^{2+} is oxidized, producing $\text{Fe}(\text{OH})_3$ and exchangeable hydrogen. This attacks the clay minerals as do other strong acids, but the aluminium and other cations released from the clay structure become exchangeable, not soluble. The silica from the clay may remain as unsupported edges of the former clay structure.

During the next period of water saturation, iron(III) hydroxides are again reduced to Fe^{2+} , part of which displaces exchangeable aluminium and other cations into the soil solution. Part of the silica in the unsupported edges is dissolved as well. Leaching water may remove some silica, as well as part of the Al and other cations, together with bicarbonate.

Because the pH rises during reduction, the aluminium still present is partly neutralized, and polymerizes into ring structures such as $\text{Al}_6(\text{OH})_{15}^{3+}$.

These form incomplete octahedral sheets in the interlayer spaces of swelling clay minerals. Such aluminium interlayers are not exchangeable; they neutralize part of the cec and block other, originally exchangeable cations in inaccessible cavities of the incomplete layer structure.

Ferrolysis thus gives rise to aluminium-interlayered materials with low cec, formed from swelling clay minerals with originally high cec, and also to amorphous silica - the latter in contrast to hydrolysis by water containing carbon dioxide. The rate of clay transformation by ferrolysis is probably an order of magnitude higher than that of hydrolysis by water with CO_2 .

Clay transformation under alkaline conditions

Where concentrations of silica and structural cations are relatively

high, mineral synthesis rather than dissolution can take place, a process also referred to as "reverse weathering".

In alkaline or neutral conditions with moderate Mg concentrations in solution, montmorillonite is stable over other clay minerals such as kaolinite or vermiculite. Montmorillonite is in fact formed in plains or valleys in humid to semiarid tropical climates, in so far as the inflow of magnesium and silica from adjoining uplands is sufficient.

Where Mg concentrations are high, as in some semiarid and arid environments, a fibrous mineral: palygorskite is formed. This contains a higher proportion of Mg than montmorillonite.

In strongly alkaline conditions with high Na concentrations in solution, analcime is formed, generally in a clay fraction dominated by montmorillonite. Because the Na in structure of this mineral is to some extent exchangeable, anomalously high exchangeable sodium percentages can be measured in such soils.

CLAY MINERALOGY AND LANDSCAPE POSITION

In different climate zones, different clay transformation processes tend to dominate: desilication in perhumid climates, reverse weathering in arid conditions, or ferrolysis on level sites in climates with a strong seasonal alternation between these two. In many climates, however, soils on crests or slopes may have a very different clay mineralogy from the valleys or plains - not because of different parent materials but because the soil hydrology gives rise to different clay transformation processes over often short distances.

The relationships between landform, hydrology, soil forming processes and clay mineralogy of wetland rice soils are summarized by Moormann and van Breemen (1978). Some examples, part extending into dryland, are discussed below.

Kaolinite and smectite

Red or brown kaolinitic soils on upland slopes alternate with black smectite clay soils in valleys or plains over extensive areas in humid to semiarid Africa and Asia. The upland soils, formed by hydrolysis by water containing carbon dioxide, are strongly to weakly acid, with low or moderate base saturation, and have a clay fraction with mainly kaolinite, often some illite, and iron(III) oxides, quartz and feldspar. The cec of the clay

fraction is uniformly low. The valley soils were formed by clay transformation under neutral or alkaline conditions, with silica and basic cations leached from the uplands. The surface horizons of these soils may have a clay fraction containing smectite, with kaolinite and illite transported from the uplands, and the with deeper horizons have mainly smectite. The smectitic valley soils are generally base saturated, tend to have a pH about neutral and have a high cec.

An early example of such a soil association in a mountain landscape on Java was described by Mohr (1944, p. 168, 162); an analyzed example from West Africa is the Shepeteri toposequence in Greenland (ed), 1981; management aspects of the Alfisols on the uplands and the Vertisols in the valleys of the Deccan plateau have been studied, e.b., by Krantz et al (1977).

Aluminium-interlayered and interstratified minerals

Where slopes are more gentle so that soils on the lower parts of the slopes become periodically water-saturated, Planosols (Albaqualfs), or less extreme surface-water gley soils, may be found between the upland and valley soils.

Such soils may have aluminium-interlayered material in the clay fraction, or interstratified minerals: these have the same general structure as smectite but show incomplete swelling because of aluminium interlayering of part of the material. These periodically wet soils, which are subject to leaching rather than accumulation as in the valleys, have low clay contents and a low cec of the clay fraction in the upper horizons; they are generally more acid than the well drained soils on steeper or higher parts of the landscape. Ferrolysis presumably is the main process that has formed the seasonally wet soils on the gentle slopes and low rises, between hydrolysis on the uplands and clay formation under neutral or alkaline conditions in the valleys or depressions.

Two such toptsequences have been studied by Bocquier (1973). One, illustrated in Fig. 1, extends from granitic upland through a gentle slope into a nearly level plain. The other toposequence appears to be virtually flat, but in fact has elevation differences up to 1 m and slopes up to 1 per cent. Even these have been enough to cause major soil and clay mineral differences as described above.

In still flatter landscapes, for example in the older river plains and low terrace landforms of Bangladesh (Brinkman, 1977), seasonally wet soils with low clay contents in surface horizons and with aluminium-interlayered

clay fractions cover most of the landscape, while perennially wet, heavy clay soils without evidence of clay destruction, occur in the depressions.

Amorphous clay minerals

In areas with recent volcanic activity, particularly on tuff, soil formation is rapid because of the large proportion of easily weatherable material in the soils. Initially, these support high silica and basic cation concentrations even during rather intensive leaching, and if the pH is high as well, smectite is formed. High runoff on steep slopes may decrease the leaching rate, so that this stage is extended. Allophane is formed rapidly from dissolved silica and polymeric octahedral Al compounds, presumably at a somewhat lower pH and lower basic cation concentrations than montmorillonite. After removal of most of the basic cations and readily dissolved silica by continued leaching, their concentrations in the soil solution become so low that kaolinite or halloysite is stable over montmorillonite. Amorphous aluminosilicates tend to crystallize and form imogolite, then halloysite, eventually kaolinite, with time aided by periodic drying out.

In a well drained toposequence on basic volcanic rocks in a perhumid climate, from near the drater of Quoin Hill, Sabah, to the bottom of the slope, Eswaran and Sys (1976 a and b) showed a trend from major proportions of allophane or related amorphous material in the clay fraction on the steep upper slope, gradually decreasing to zero in the oldest soils on a more gentle slope downhill. Smectite decreased from major on the upper slope to near zero on the mid-slope; kaolinite and halloysite increased downhill from minor proportions to dominant in the oldest soils.

A variant of this toposequence can be found from Mount Makiling to Los Banos, Philippines. The highest part of the slope has typical Andisols, with probably mainly amorphous materials in the clay fraction. A lahar (a former mudflow) of the same origin constituting the upper part of the IRRI farm has soils similar to the mid-slope soil at Quoin Hill, but the adjacent plain in which the lower part of the IRRI farm is located, which contains materials of the same origin, has imperfectly drained swelling clay soils - presumably the result of clay transformation under high concentrations of silica and basic cations in the drainage water from the adjacent upland.

SURFACE VERSUS BULK COMPOSITION OF CLAY FRACTIONS

The mineralogical composition of clay fraction generally is the result of long-term processes and does not change quickly with a change in circumstances. However, the surface properties of a particle in the clay fraction are not necessarily in equilibrium with its bulk composition. Surface properties are modified relatively quickly when external circumstances change, and surface rather than bulk properties are generally of primary importance for physical chemistry: for the fertility, toxicity, and other management aspects of soils. Herbillon (1981), e.g., has summarized the nature and properties of clay and oxide surfaces.

Iron oxides

Soils with kaolinitic clay fractions containing less than about 12 percent Fe_2O_3 generally have the properties associated with kaolinite: low, pH-dependent cec, low structure stability, consequent erodibility and tendency to become dense when mechanically disturbed by traffic or rain impact, moderate phosphate buffering capacity and fixation.

In kaolinitic soils with contents of free iron oxides exceeding 12 percent of the clay fraction, the clay tends to have an oxide surface. Such soils then have very low cec, high structure stability and generally severe phosphate fixation. The percentage quoted is variable, however, depending on the nature and distribution of the oxides.

In smectite soils, too, there is a major distinction in structure stability and in the degree to which a granular or fine blocky surface structure can be restored by drying. The Chromic Vertisols, with relatively high contents of free iron oxides, have favourable properties in this regard, while the Pellic Vertisols do not. There may be other causative factors as well besides the content and distribution of iron oxides.

Other substances or bonding agents

Structural stability in some soils may be due to other surface features of the clay fraction besides organic matter, oxidic surfaces or polyvalent exchangeable cations. Besides finely dispersed iron oxides, features identified by Butler et al (1976) in Australia include the presence of a fine clay fraction strongly bonded or cemented into silt-sized aggregates, probably

mainly at edges of clay packets rather than on planar faces. Silica cementation is possible but has not been proved in these soils. Intergrowth of clay mineral crystals may also be a factor, as well as the large electrostatic interaction between clay layers with a high charge density.

Kaolinite corrosion and subsequent cementation has also been suggested as a cause for anomalously high structural stability in certain Oxisols (Coughlan et al, 1973 and Herbillon et al, 1966).

In clay fractions of Kenyan soils with amorphous material Wielemaker (1984) found indications that the cec at a given pH is higher with even minor increases in the ratio of extractable amorphous Si to Al and Si to Fe. He also modified the charge characteristics experimentally with applications of amorphous silica. Similar amorphous silica-iron compounds with some aluminium cover the surfaces of crystalline clay minerals in clay soils over large areas in Quebec and Ontario, Canada. These soil are very stiff in place, but may become virtually liquid when extensively sheared (McKyes et al, 1974), even though the content of amorphous material is only 10-12 percent.

Rapid changes in surface properties

The most rapid changes in surface properties and physical chemistry of soils are brought about by alternating reduction and oxidation. The processes occurring during soil reduction have been extensively dealt with by Ponnamparuma (1972).

During reduction, iron(III) oxides are converted into soluble and exchangeable Fe^{2+} , with a concurrent rise in pH. In neutral soils with smectite or vermiculite in the clay fraction, this may give rise to synthesis of materials with a structure similar to smectite and containing Fe(II) in the octahedral sheet. Where such soils remain perennially wet, zinc tends to be fixed in a form unavailable to wetland rice: I suspect because it can be built into the octahedral positions of the synthesized material. Upon reoxidation, the zinc becomes available again, which suggests that the material is only stable in reduced conditions - presumably because of its high Fe(II) content.

In acid soils, particularly those with a kaolinitic clay mineralogy, soluble Fe^{2+} concentrations tend to rise to high levels because of the low cec and because conditions are unfavourable for precipitation of iron(II) oxides or carbonates or synthesis of silicates. Then, the iron toxicity syndrome may be observed in wetland rice, depending on the Fe^{2+} concentration in relation

to the concentrations of nutrient cations and phosphate availability.

When a reduced soil is oxidized again, the Fe^{2+} is converted into $\text{Fe}(\text{OH})_3$. The original iron oxides are thus distributed in a different way, and with a generally higher specific surface and activity. In high-activity clay soils, this may increase the stability of a structure established before inundation, as in flood following of sugarcane land in the Guyana coastal plain, or of a structure established just before oxidation, as in land preparation for wheat after rice in the Jangtze delta, China. In low-activity clay soils, the effects of alternate reduction and oxidation are less clearly beneficial, in part because the removal by leaching of nutrient cations tends to be accelerated in periodically reduced conditions.

In soils with high amounts of active iron or aluminium, for example with amorphous, halloysitic or oxidic clay fractions, phosphate fixation is severe and cec may be low or very low. Phosphate or silica on the surface of such materials drastically changes their properties. Although very high phosphate applications to decrease or eliminate phosphate fixation may not be economic in most cases, they are effective and rapid. The use of silica or finely ground silicates may be more economic. This, too, tends to lower the amount and severity of phosphate fixation and raises the cec at a given pH. Substances that could be tried include wollastonite (Ca silicate), used as a silica fertilizer in some wetland rice areas, or ground feldspar, or basic slag, containing phosphate and silicate.

In practice, Ca silicate applications on a Gibbsiumox in Hawaii gave disappointing results, but the high P fixing capacity in Oxisols was reduced by long-term irrigation with water containing 30 mg Si per liter (Fox, 1980). This resulted in a tripling of water-soluble Si from 1.6 to 5.3 mg/l, increase in poorly crystalline soil Si from 730 to 1360 mg/kg, and a drop in P sorption (at 0.2 mg/l solution concentration) from 235 to 100 mg/kg, all compared with the soil that received low-Si irrigation water.

Experiments by Jepson et al (1976) indicate that silica reacts with a gibbsite ($\text{Al}(\text{OH})_3$) surface in quantities from less than a monolayer at pH 4 to more than that at pH 9, with an increase in cation exchange capacity and decreases in anion exchange capacity and Al solubility at a given pH.

These different findings can probably be summarized in the estimate that silication of oxidic surfaces is feasible, but that the process works much more slowly in soils than in laboratory situations because of imperfect mixing

and slow diffusion of silica to the oxidic surfaces - probably over several crop seasons.

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Table 1. Some chemical and physical properties of soils with clay fractions dominated by different materials.

Dominant material in clay fraction or on surface	Properties				
	cec	K or NH ₄ fixation	phosphate fixation	swell-shrink ratio	physical stability
vermiculite	v. high	high	-	mod.	mod.
beidellite	high	high	-	high	mod.
montmorillonite, nontronite	high	-	-	high	mod.
illite	mod.	low	-	mod.	mod.
kaolinite, halloysite	low*	-	high	-	low
allophane, imogolite	v. high*	-	v. high	mod./low	mod.**
Fe, Al oxides and hydroxides	v. low*	-	high/ v. high		high
Al-interlayered clays	low*	-	high	mod./-	mod.

* pH-dependent

- not significant

** high against rainfall or water erosion; allophane soils low under load