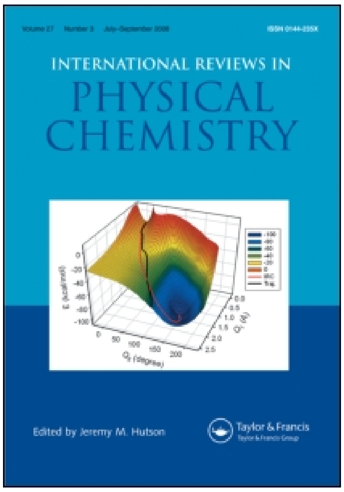

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The effect of tetrahedral substitution of Si by Al on the surface acidity of the oxygen plane of clay minerals

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Oxygen planes of clay minerals are formed by a continuous linkage of $[SiO_4]^{4-}$ tetrahedra. This plane determines many of the clay colloidal and surface properties. The d_π–p_π bond between O and Si in Si–O–Si and Si–O–Al groups is described here according to the valence bond treatment. Partial π interaction between O and Si causes the O atom to serve as a weak base. Tetrahedral substitution of Si by Al leads to changes in the clay surface properties, resulting from an increase in the basic strength of the siloxanes. Substitution of Mg by Al in octahedral sheets increases the polarization of the OH planes. Interlayer hydrogen bonds between oxygens and hydroxyls were detected in substituted serpentines and chlorites. Wettability of tetrahedral–octahedral–tetrahedral (TOT) clay minerals was determined from advancing contact angles of water. This angle decreased with increasing degree of tetrahedral substitution, indicating an increase in strength of hydrogen bonds between water and the oxygen plane, due to an increase in its basic strength. Hydrogen bonded water may serve as bridges between parallel layers and, consequently, the swelling of TOT minerals with tetrahedral substitution is prevented to some extent. Interactions occurring between the oxygen plane and acid sites in the interlayer space of smectites and vermiculites affect the bulk surface acidity of the interlayer and the type of reactions which occur between the clay and adsorbed organic acids and bases. Clays with tetrahedral substitution form π bonds by donating electrons to aromatic cations and radicals.

1. Introduction

The surface acidity of a clay mineral is responsible for many of its colloidal properties, and its readiness to be dispersed in various media and to adsorb different ions and molecules. The catalytic activity of different clay minerals, which is very important for many natural and industrial processes, is determined by their surface acidity. Acidic and basic sites of different natures and with different strengths, appear together on the clay surface, and they determine the bulk acidity of the mineral. In previous publications on surface acidity the exchangeable metallic cations and their hydration spheres, or the broken-bonds functional groups (e.g. Si–OH and Al–OH) as sites for acid–base reactions were extensively treated (Mortland and Raman 1968, Theng 1974, Yariv and Cross 1979). In the present review the surface acidity of the oxygen plane of clay minerals will be treated. Being rich with lone-pair electrons, the oxygen plane is basic. In the present review we shall demonstrate how the basic strength of this plane is changed as a result of the tetrahedral substitution.

2. Structure of clay minerals

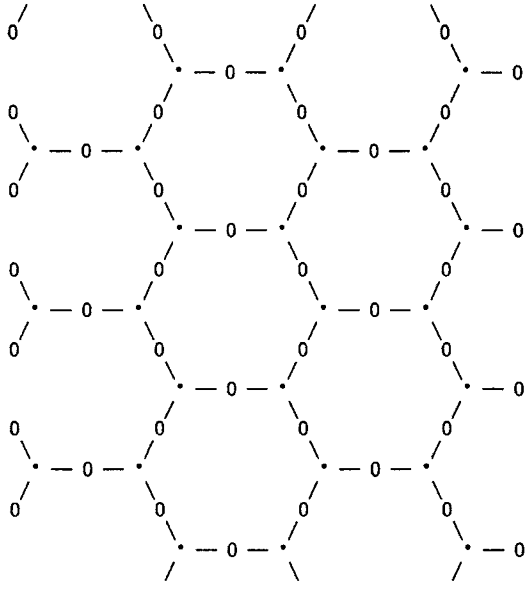
Clay minerals are essentially hydrous layer aluminosilicates (phyllosilicates), with magnesium and iron acting as proxy wholly or in part for the aluminium in some of the minerals and with alkali metals and alkaline earth metals present as essential constituents in some of them. Magnesium or alumino-silicate layers are essentially composed from two types of sheets, a tetrahedral and an octahedral, designated as T and O, respectively. Each sheet is composed of planes of atoms, arranged one above the other, a plane of oxygens above a plane of silicons, aluminiums or magnesiums, and the latter above another plane of oxygens, and so on (Grim 1968).

Structures of clay minerals which are mentioned in the present review, are described in the following sections.

2.1. *The tetrahedral sheet*

A continuous linkage of $[SiO_4]^{4-}$ tetrahedra by the sharing of three O atoms with three adjacent tetrahedra produces a sheet with a planar network (scheme 1). In such a sheet the silica tetrahedral groups are arranged to form a hexagonal network, which is repeated indefinitely to form a layer of composition $[Si_4O_{10}]^{4-}$. The tetrahedra are arranged so that all their apices point in the same direction, and all their bases are in the same plane. In this plane the oxygens form an open hexagonal network which is often referred to as 'the oxygen plane', 'the hexagonal plane' or 'the perforated plane of oxygens'. In fact, the silicon tetrahedra are slightly distorted and consequently the cavities which are bordered by six oxygens are ditrigonal rather than hexagonal (Radoslovich and Norrish 1962). This perforated plane of oxygens is an important contributor to the surface properties of the clay minerals. Each oxygen of this plane is covalently bound to two silicons, thus playing the active component of an Si–O–Si (siloxane) group.

Silicon atoms in the tetrahedral sheet can be replaced by aluminium atoms. Substitution of Al for Si contributes a negative charge to the tetrahedral sheet. In many minerals this substitution is very small but in micas 25% of the possible silicon sites are



Scheme 1. The tetrahedral sheet, top view. Types of linkage of silicon–oxygen tetrahedra. (O) are oxygen atoms which form the oxygen plane. (·) are silicon atoms which form the silicon plane lying above the oxygen plane.

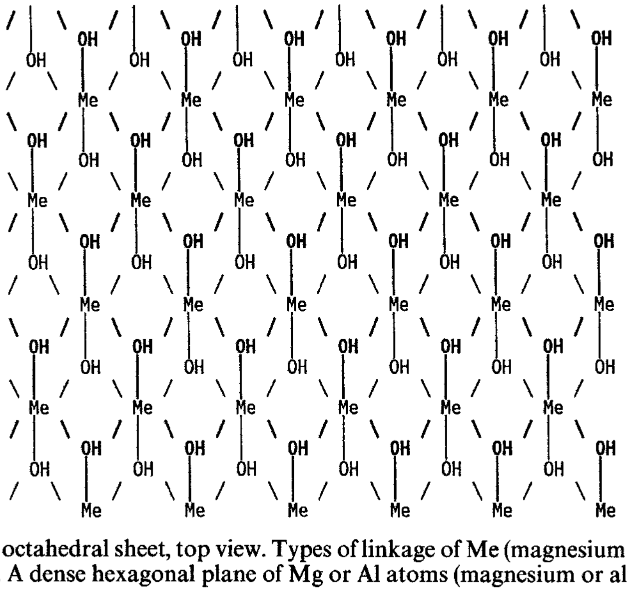
substituted by Al. As we will show later the substitution of Al for Si changes the surface properties of the perforated oxygen plane, since Si–O–Al groups are better donors of electron pairs than Si–O–Si groups.

No clay mineral has been found in nature with tetrahedral substitution of Si by P. By applying the valence bond (VB) treatment for the Si–O bond, Yariv (1987) demonstrated that such a substitution cannot take place in layer silicates.

2.2. *The octahedral sheet*

Such a sheet is obtained by the condensation of single $[Mg(OH)_6]^{4-}$ or $[Al(OH)_6]^{3-}$ octahedra (scheme 2). Each O atom is shared by three octahedra, but two octahedra can share only two neighbouring O atoms. In this sheet the octahedra are arranged to form a hexagonal network, which is repeated indefinitely to form a layer of composition $[Mg_6O_{12}]^{12-}$ or $[Al_4O_{12}]^{12-}$. The minerals brucite $Mg(OH)_2$ and gibbsite $Al(OH)_3$ have such a sheet structure. This sheet structure is densely packed being composed of a dense hexagonal plane of Mg or Al atoms sandwiched between two dense hexagonal planes of hydroxyls. The latter is named 'the hydroxyl plane'. All the octahedra are filled with Mg atoms in brucite or in its clay derivatives, but only 2/3 of the octahedra is filled with Al atoms in gibbsite and in its clay derivatives. Derivatives of brucite and gibbsite are called tri and dioctahedral clay minerals, respectively. In some clay minerals the hydroxyl plane is an important contributor to the surface properties of the mineral.

Aluminium atoms in the octahedral sheet of a dioctahedral mineral can be replaced by iron or magnesium atoms. Similarly, magnesium atoms in a trioctahedral mineral can be replaced by trivalent aluminium, di or trivalent iron and by monovalent lithium atoms. Substitution of a trivalent cation by a divalent cation or a divalent one by a monovalent cation contributes a negative charge to the octahedral sheet.



Scheme 2. The octahedral sheet, top view. Types of linkage of Me (magnesium or aluminium)–hydroxyls. A dense hexagonal plane of Mg or Al atoms (magnesium or aluminium plane, respectively) is sandwiched between two dense hexagonal planes of hydroxyls (hydroxyl plane). Dark and light OH hydroxyls which form the hydroxyl plane lying above and under the magnesium or aluminium plane, respectively.

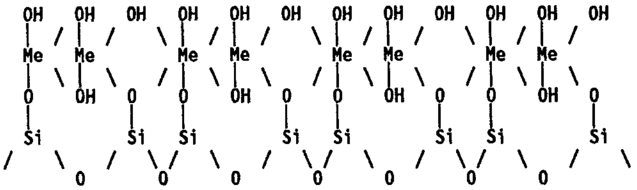
2.3. *The TO type layer silicates*

Minerals of the serpentine–kaolin group are composed of a single tetrahedral sheet condensed with a single octahedral sheet into one unit layer designated by 1 : 1 or by TO. In this unit layer the apices of the silica tetrahedra and one of the OH planes together form a single plane that becomes common to both tetrahedral and octahedral sheets. Two thirds of the O atoms in the common plane are shared by Si and Mg or Al atoms and the remainder are shared by protons and Mg or Al atoms. In serpentine the octahedral sheet is brucitic whereas in kaolinite it is a gibbsite-like layer (scheme 3). The ideal structural formulae of layers of serpentine and kaolinite are $[Mg_6Si_4O_{10}](OH)_8$ and $[Al_4Si_4O_{10}](OH)_8$, respectively.

In trioctahedral minerals the O–H vector is perpendicular to the octahedral sheet. In dioctahedral minerals the situation is more complicated. For example, in kaolinite the O–H vector makes an angle of 34° with the 001 plane, away from the octahedral sheet, and the projection of the vector on to (001) is at ~30° to the axis (Adams 1983).

The minerals of the kaolin subgroup consist of dioctahedral layers continuous in the *a* and *b* directions and stacked one above the other in the *c* direction. The variation between members of this subgroup consists mainly in the way in which the TO unit layers are stacked one above the other. In the tactoid which consists of several stacked TO layers, one differentiates between inner-surface, inner and surface hydroxyls. Inner hydroxyls are OH belonging to the O, OH plane which is obtained by the condensation of the tetrahedral and octahedral sheets. Inner-surface and surface hydroxyls are OH belonging to the hydroxyl plane which did not take part in the condensation of the two sheets. Surface hydroxyls are OH belonging to the plane which forms the external surface of the tactoid whereas the inner-surface hydroxyls are OH belonging to the hydroxyl plane which forms the surface of the TO layer but is located inside the tactoid. In the same manner, surface oxygens are O belonging to the plane which forms the external surface of the tactoid whereas the inner-surface oxygens are O belonging to the oxygen plane which forms the surface of the TO layer but is located inside the tactoid.

These minerals expose surfaces of oxygens and hydroxyls. For most kaolinites a specific surface area of about 10 $m^2 g^{-1}$ was determined. The edges of kaolinite usually comprise 15–20% of its total area, and thus the two surfaces of oxygens and hydroxyls should each make about 40% of the external surface (Kronberg *et al.* 1986). In halloysite parallel TO unit layers are separated by a water monolayer. Yariv and Shoval (1975, 1976) showed that there are no hydrogen bonds between water molecules and the O or OH planes of the halloysite. The negative oxygens of the water molecules in the adsorbed monolayer are oriented toward the hydroxyl plane whereas the positive hydrogens are oriented towards the oxygen plane, but there are no localized interactions between water molecules and the inner surface planes. Intermolecular hydrogen bonds occur between the water molecules. Some of the minerals of the



Scheme 3. Linkages in the TO type (1 : 1) layer silicate (Me = magnesium or aluminium), side view.

serpentine subgroup, e.g. lizardite, show a stacking of continuous trioctahedral layers similar to that of kaolinite. In the case of chrysotile the trioctahedral extending TO unit layer is rolled up and a tubular fibre is obtained from this spiral rolling. This mineral exposes surfaces of hydroxyls.

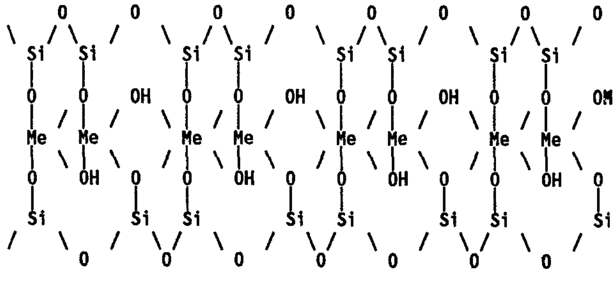
2.4. *The TOT type layer silicates*

2.4.1. *Talc and pyrophyllite*

Minerals of the talc–pyrophyllite group are composed of two tetrahedral sheets condensed to a central octahedral sheet forming one unit layer designated by 2 : 1 or by tetrahedral–octahedral–tetrahedral (TOT) (scheme 4). The sheets are combined so that the apices of the tetrahedra of each Si sheet and one of the hydroxyl planes of the octahedral sheet form a plane common to both sheets. Two common planes are obtained on both sides of the octahedral sheet. These common planes are the same as the common plane obtained for the serpentine–kaolin group. The ideal structural formula of layers of talc and pyrophyllite are $[Mg_6Si_8O_{20}](OH)_4$ and $[Al_4Si_8O_{20}](OH)_4$, respectively. A crystal of the mineral consists of TOT layers continuous in the *a* and *b* directions and stacked one above the other in the *c* direction. The layers are held together by van der Waals attractions. These minerals expose perforated oxygen planes which are highly hydrophobic.

2.4.2. *Smectites and vermiculites*

Minerals of the smectite and vermiculite groups (the former known sometimes as the montmorillonite group) also consist of TOT layers. They differ from talc and pyrophyllite in that a small fraction of the tetrahedral Si atoms is substituted by Al atoms, and/or octahedral atoms (Al or Mg) are substituted by atoms with lower oxidation numbers. The resulting charge deficiency is balanced by exchangeable cations, in smectites mainly Na, Ca and Mg and in vermiculite Mg, which are located between parallel layers. The negative charge per unit cell from isomorphous substitution ranges between 0·5 and 1·3 electron charges in smectites and 1·1–2·0 electron charges in vermiculite. Water and other polar molecules may penetrate between the layers causing the expansion of the structure in a direction perpendicular to the layers. Beidellite and saponite are di and trioctahedral smectites, respectively, with mainly tetrahedral substitution whereas montmorillonite and hectorite are di and trioctahedral smectites, respectively, with mainly octahedral substitution. Montmorillonite is the most common smectite mineral. Vermiculites usually have greater layer charge densities than smectites and the charge originates mainly from



Scheme 4. Linkages in the TOT type (2:1) layer silicate (Me = magnesium or aluminium), side view.

tetrahedral substitution. For both groups interior specific surface area of about 750–800 $m^2 g^{-1}$ on the oxygen cleavage planes, was determined. The exterior surface area for most natural smectites is less than 20% of the interior surface area whereas the total exterior surface area for most natural vermiculites is not more than a few $m^2 g^{-1}$.

2.4.3. *Sepiolite and polygorskite*

Sepiolite and polygorskite are unique among the TOT clay minerals in having channel structure. This structure is obtained from the repeated inversion of the silicate layer. The two minerals differ in the frequency of inversion, sepiolite having wider channels.

3. Basic properties of the oxygen plane

Basicity of the oxygen plane of the silicate layer is determined by possible interactions between the O atoms of the siloxane groups and acidic species which tend to accept electron pairs. The acid can be of either Bronsted or Lewis type. For this to happen the siloxane oxygen atom must donate a lone pair of electrons to an acceptor. Only non-bonding hybridized orbitals are able to serve as sites for electron pair donation, because in the hybridized orbital the electron density is high on one side of the O nucleus and this orbital may essentially overlap with orbitals of the acidic moiety, whereas in a non-hybridized orbital the lone pair electrons are equally distributed on both sides of the nucleus.

In covalent compounds of oxygen one would expect that the oxygen atom would undergo an sp^3 hybridization giving rise to four equal hybridized orbitals with a minimum repulsion between the four electron pairs which fill the valence shell of this oxygen. This hybridization permits two non-bonding hybridized orbitals with lone-pair electrons to serve as proton acceptors, in addition to the two σ bonding orbitals. Theoretically, an sp^3 hybridization should result in an Si–O–Si angle slightly smaller than 109°, as found in H_2O molecules.

Determination of Si–O–Si angles in different silicates revealed that this angle ranges between 120–180°. In most silicates the value of 139–140° was determined (Liebau 1985). An angle of 180 or 120° is an indication of an sp or sp^2 hybridization on the oxygen atom, respectively (figure 1). If the angle ranges between these values it should be due to a resonance of two canonical structures, one with sp and one with sp^2 hybridization on the oxygen atom. The basic strength of the oxygen plane decreases with decreasing electron density in the non-bonding hybridized orbitals and consequently sp^2 hybridization on the oxygen decreases basicity compared with sp^3 whereas sp hybridization leads to the abolition of basicity. To conclude, the Si–O–Si angle can give information on the basic strength of a siloxane group, this strength increasing with decreasing Si–O–Si angle. In the following Section we will show that hybridizations sp and sp^2 on the O atom occur to enable this element to be involved in a d_π–p_π bond.

3.1. *The* d_π–p_π *bond*

The elements of the third row of the periodic table are characterized by the involvement of the d_π–p_π bond in the overall bonding system (Cruickshank 1961, 1985). This bond has been found to occur between Si, P, S or Cl and N, O or F from the second row of the periodic table. As the d orbitals have a considerable sideways extension, they can overlap with p orbitals on the second atom to form π bonds. However, as the d

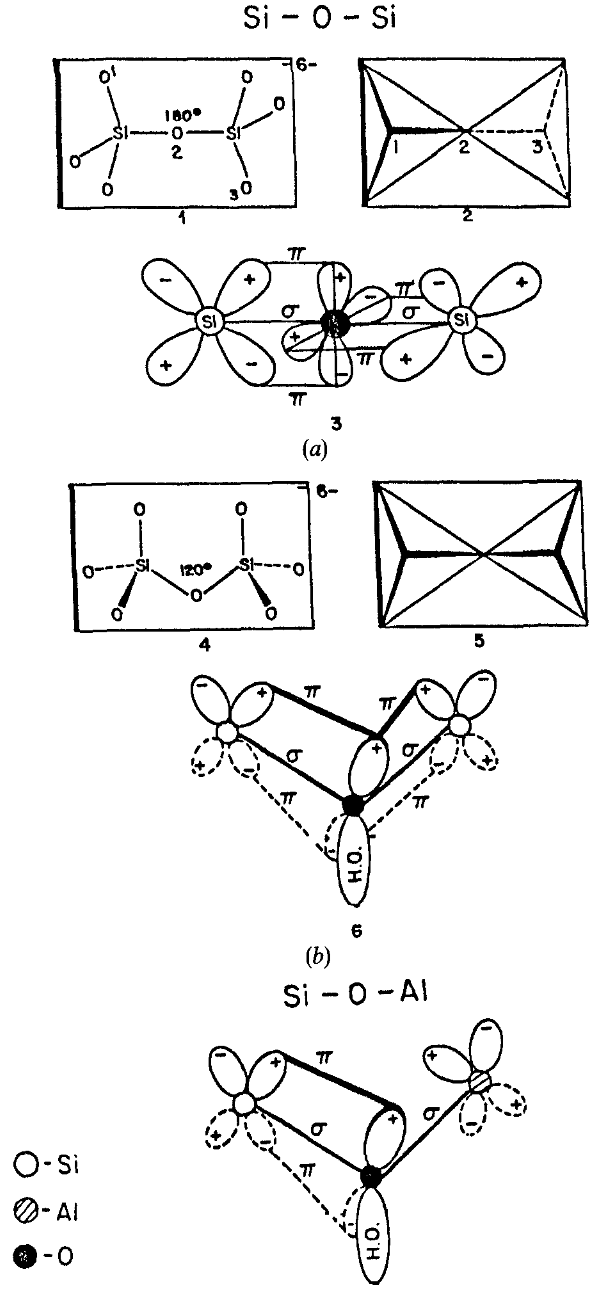


Figure 1. (*a*) and (*b*) Two canonical structures of a siloxane group giving rise to an angle ranging between 120 and 180°. (1–3) and (4–6) sp and sp^2 hybridizations, respectively, on the O atom of an Si–O–Si group. (3) and (6) Bonding orbitals between oxygen and silicon (σ and π) and atomic orbitals (+ – and H.O.) in Si–O–Si groups in exposed surfaces of tetrahedral sheets of layer silicates. (*c*) Bonding and atomic orbitals in Si–O–Al groups (sp^2 hybridization) in exposed surfaces of tetrahedral sheets of layer silicates. (H.O. is an abbreviation for hybridized atomic orbital of oxygen with a lone pair of electrons; (+ –) non-hybridized atomic orbitals of oxygen (2p orbitals) and of silicon or aluminium (3d orbitals)).

orbitals are of higher energy than the p orbitals, d orbitals are used in π bonding mainly to active ligands such as N, O or F, and π bonds involving d orbitals probably add less on average to overall stability of the bond than does the p_π–p_π bonding of the second row elements. In the formation of this bond, silicon, which has empty d orbitals, serves as an acceptor of electron pairs and the element of the second row, which has a higher electron density in its valence shell, serves as a donor of electron pair. Since this bonding is an addition to the σ bonding, the Si–O bond is considered to have a partial double bond character.

The first three elements in the third row of the periodic table (Na, Mg and Al) do not take part in the d_π–p_π bondings. These elements also have empty 3d orbitals. However, low charges of their nuclei, compared to those of Si, P, S or Cl, lead to their behaviour as weak acids, so that their empty 3d orbitals do not accept 2p electron pairs from N, O or F atoms. Similarly, the first four elements of the second row (Li, Be, B and C) do not take part in d_π–p_π bondings. Atoms of these elements have relatively low electron densities in their valence shells and do not donate electron pairs to form this kind of bonding.

3.2. *The effect of tetrahedral substitution on the surface acidity of siloxanes*

Siloxanes are unreactive. The strong bond between the Si and O atoms and the partial π interaction cause the oxygen to lose much of its basicity and to show extremely little tendency to donate an electron pair. There is much evidence showing that tetrahedral substitution of Si by Al leads to an increase in both types of surface activity, acceptance and donation of electron pairs. The increase in acidic activity is explained by the presence of additional exchangeable cations. The increase in basic strength of the siloxanes can be explained in the VB treatment either with the inductive effect model or with the Si–O bonding model.

3.2.1. *Acid sites and Si–O–Al groups in clay minerals*

The isomorphous substitution of a trivalent Al for a tetravalent Si in the tetrahedral silicate sheet results in excess negative charge in the oxide anion lattice. To maintain electrical neutrality the silica–alumina particle must gain exchangeable cations in the diffuse layer. The nature and strength of the surface acidity depends on the nature of the exchangeable cations. Non-hydrated metallic cations are Lewis acid sites. The acid strength increases with the charge of the cation and decreases with increasing cation size. If the exchangeable cations are protons, organic ammonium cations or hydrated metallic cations, Bronsted acid sites are obtained. Since the electrostatic attraction forces between the protons and the huge negative double-oxide anion species are weak, the acid strength of these Bronsted acid sites is higher than that of broken-bond surface silanols (Yariv and Cross 1979).

3.2.2. *The inductive effect model and the basic strength of Si–O–Si and Si–O–Al groups in clay minerals*

The non-bonding lone-pair electrons on the oxygens are repelled by the electrons bonding between the oxygen and the silicons. The more strongly they are repelled, the stronger will be the basic strength of the oxygen plane. In fact, each pair of bonding electrons is attracted by both nuclei, that of O and that of Si and the average distance between this pair and the nucleus of O, as well as the degree of repulsion between them and the non-bonding electrons, is the result of these two attractions. When Si of the

(*a*) (*b*)

Figure 2. Inductive effects of siloxane groups, Si–O–Si (*a*) and of alumino–siloxane groups, (Si, Al)–O–(Si, Al), (*b*) on the electron donation ability of a bridging oxygen and the contribution of these inductions to the basic strength of the oxygen plane. The strength of the induction is shown semi-quantitatively by arrows.

siloxane group is replaced by the less electronegative element Al, on average the Al–O bonding electrons are nearer the O nucleus compared with Si–O bonding electrons. Consequently the repulsion between bonding and non-bonding electron pairs increases, donation of non-bonding electron pairs becomes favourable and the basic strength of the oxygen plane increases (figure 2).

3.2.3. *The double bond character of the Si–O bond and the basic strength of Si–O–Si and Si–O–Al groups in clay minerals*

As was mentioned in Section 2.1., the coordination number of Si in clay minerals is four, involving sp^3 hybridization. Three of the oxygens which coordinate the silicon atom belong to the 'perforated oxygen plane', whereas the fourth oxygen atom belongs to the 'O, OH plane', which is common to the tetrahedral and octahedral sheets. The Si atom uses vacant d orbitals to form π bonds with O atoms.

Oxygens which belong to the 'perforated O plane', are the major contributors to the d_π–p_π bonding system. Each O atom requires one or two non-hybridized p orbitals in order to form π bonds with one or two Si atoms, respectively. Consequently, the bridging O atoms in a siloxane group would be expected to show sp or sp^2 hybridization giving rise to Si–O–Si angles of 180 or 120°, respectively. An sp hybridization enables two p orbitals of an O atom to overlap with d orbitals of two Si atoms. Two Si–O double bonds are obtained, each consisting of a σ and a localized π orbital. An sp^2 hybridization enables only one p orbital of an O atom to overlap with d orbitals of two Si atoms. These three atomic orbitals overlap to form a three centred π bond orbital. The π bond order in the three centred bond is less than in the localized two centred π bond.

Very little information is available from the literature on X-ray determinations of the Si–O–Si angle in clay minerals. Lee and Guggenheim (1981) observed that the Si–O–Si angle in pyrophyllite was equal to $\approx 136°$. From this data it can be concluded that the pyrophyllite structure results from two canonic structures with sp and sp^2 hybridizations on the O atom, and that the latter makes the principal contribution to the resonance in the double bond system.

Lin and Guggenheim (1983) studied the structure of a brittle mica where almost 50% of the tetrahedral Si was substituted by Al or Be, which do not participate in a d_π–p_π bond. They found that the Si–O–Al (or Be) angle was equal to 120·9°. From their observation it can be concluded that in this mineral the O is involved in an sp^2 hybridization only. According to our assumption about the double bond character of the Si–O bond in the siloxanes, the difference between the two samples can be attributed to the substitution of Si by Al or Be. In the brittle mica each O atom in the 'perforated O plane' is simultaneously bound to one Si and one Al (or Be) atom. The Si–O bond consists of a σ and a localized π orbital, whereas the Al–O (or Be–O) bond is a pure π bond and does not use a non-hybridized p orbital of the oxygen. In this case O atoms undergo sp^2 hybridization in order to minimize repulsion between bonding and non-bonding electrons in the valence shell. According to the present model, the basic strength of the oxygen plane of brittle mica should be higher compared with that of pyrophyllite. This is demonstrated in figure 1 showing that the electron density in the non-bonding orbital of an oxygen belonging to the 'perforated oxygen plane' is higher in the Si–O–Al group, where the O undergoes an sp^2 hybridization, compared with an Si–O–Si group, where the O undergoes a resonance of sp and sp^2 hybridizations.

3.3. *Basic strength of the oxygen plane in di and trioctahedral clays*

The hybridization in which an O atom, which bridges between the tetrahedral and octahedral sheets is involved, depends on whether the clay is di or trioctahedral. In a trioctahedral clay, where this oxygen is coordinated by four atoms (one Si and three Mg), it is involved in an sp^3 hybridization and has no contribution to a d_π–p_π bond. On the other hand, in a dioctahedral clay, where this oxygen is coordinated by three atoms (one Si and two Al) it is involved to some extent in an sp^2 hybridization and has a small contribution to a d_π–p_π bond with the Si. Consequently, the contribution of the oxygens from the oxygen plane to the π system decreases and the electron density at the non-bonding orbitals becomes higher, compared to their density at non-bonding orbitals of trioctahedral clays. It is concluded that the basic strength of the oxygen plane of dioctahedral clays (kaolin-type group), although weak, is higher than that of trioctahedral clays (serpentines).

3.3.1. *Intercalation complexes of kaolin-group minerals*

Minerals from the kaolin group can intercalate certain inorganic salts and a variety of organic compounds (see e.g. Wada (1961), Weiss (1961), Weiss *et al.* (1963), Carr and Chih (1971), Theng (1974)). The salts or organic compounds penetrate the interlayer space of kaolin-like layers and so expand the crystal from a basal spacing of $\approx 0{\cdot}72$ nm to about 1·00–1·44 nm. The penetrating species that break the strong electrostatic species and van der Waals types of interactions between the layers may form hydrogen bonds with surface hydroxyls, as was first inferred by comparing calculated and experimental basal spacings, and later confirmed by infrared spectroscopy. The inner-surface O–H and Al–OH i.r. stretching vibrations of the kaolinite are perturbed and are shifted to lower wavenumbers. Also the characteristic absorption bands of the adsorbed proton acceptor groups are shifted (see e.g. Ledoux and White (1964, 1966 *a*, *b*), Cruz *et al.* (1969), Olejnik *et al.* (1971 *a*, *b*, *c*)). Strong proton donors, such as an NH_2 group in urea or in amide, may form hydrogen bonds with oxygens located on the tetrahedral sheet surface. Since the oxygen plane is a very poor electron donor, these hydrogen bonds are very weak, but can be identified from perturbation of the Si–O–Si stretching vibrations of the kaolinite (see e.g., Yariv (1975, 1986 *b*), Michaelian *et al.* (1991)).

All experiments to intercalate serpentine type minerals failed. The difference in the behaviour between dioctahedral and trioctahedral groups results from the difference in the basic and acidic strengths of the oxygen and hydroxyl planes. In serpentines no hydrogen bonds can be formed between the intercalating compound and the oxygen or hydroxyl planes because of their extremely weak basic or acidic strength, respectively.

3.3.2. *Inversion of silicate layers in antigorite, sepiolite and palygorskite*

Antigorite (a serpentine sub-group mineral), sepiolite and palygorskite show an occasional inversion of the silicate layer with Si–O–Si groups which serve as bridges between the alternating ribbons of alumino–Mg–silicates. An Si–O–Si angle of ≈ 180° is supposed to be found in these bridging groups (Bradley 1940, Kunze 1961). The double bond character of both Si–O bonds in this siloxane group is revealed from an i.r. absorption band at ≈ $1200\,\mathrm{cm}^{-1}$ (Yariv 1986*a*), proving that these bonds have a very high π bond order. This kind of inversion has been found in nature with trioctahedral clays where only three of the four coordinating oxygens contribute to the π system of the silicon. It has not been found with the dioctahedral clays, where all four coordinating oxygens contribute to the π system of the silicon. In the case of silicon, an Si–O bond with a very high π bond order, as the one which involves an sp hybridization, can be obtained only if some of the other Si–O bonds have a very small π bond order or have no π contribution at all, as is the case with the trioctahedral clays.

Oxygens belonging to siloxane groups of this type, cannot have basic properties, because the two electron pairs which are not involved in σ bonds, are involved in π bonds.

In sepiolite and palygorskite 'bound water' are water molecules inside the channels, which are coordinated to Mg exposed at the edges of the octahedral framework. Several authors suggested that these molecules form hydrogen bonds with the O atoms which are located at the inversion sites of these minerals (see e.g. Serna *et al.* (1977 a)). According to the present model water molecules cannot form hydrogen bonds with these oxygens.

4. Interlayer hydrogen bonds between oxygens and hydroxyls in clay minerals with tetrahedral substitution

In clay minerals the hydroxyl plane may serve as a proton donor and one would expect that in TO minerals and in chlorite the interactions between the inner surface hydroxyl plane and inner oxygen plane may give rise to hydrogen bonds. To understand the nature of this interaction, we shall first summarize present knowledge about hydrogen bonds in general (Jeffrey and Seanger 1991) and relate this to hydrogen bonds in which siloxane groups are involved. A pragmatic definition of a hydrogen bond says that this bond exists when the distance between the hydrogen and the acceptor atom is shorter by at least 0·02 nm than the sum of the van der Waals contact radii (Hamilton and Ibers 1968). According to Pauling (1939), a hydrogen bond between the donor covalent pair X–H (in which a hydrogen atom, H, is bound to a more electronegative atom X) and another non-covalently bound nearest neighbour electronegative acceptor atom *B* (in the polar species *AB*), results from electrostatic attraction. In the direction of the X–H bond, the proton is increasingly descreened as the electronegativity of X increases (e.g. proceeding from carbon to fluorine) and the electric potential on H is increasingly positive. This gives rise to a dipole with positive charge at the hydrogen end of the X–H bond. It is the Coulombic interaction of the dipole with the excess electron density at the acceptor atoms that forms the hydrogen bond interaction, as follows:

$$\overset{\delta-}{\mathrm{X}}-\overset{\delta+}{\mathrm{H}}\cdots\cdots\overset{\delta-}{B}-\overset{\delta+}{A}.$$

There is some directional character to the hydrogen bond which, however, is much less pronounced than in covalent bonding, especially for the moderate to weak hydrogen bonds, where the interaction is primarily Coulombic.

Very strong hydrogen bonds, such as $F\text{–}H\cdots F^{-}$, are formed when X is an exceedingly electronegative atom and B has an exceptionally large excess of electron charge. In this case the structural distinction between the covalent F–H and the $H\cdots F$ hydrogen bond disappears, since the hydrogen atom lies at or close to the mid-point of the $F\cdots F$ line of centres. The bond lengths $H\cdots B \approx X\text{–}H$ and the bond angle $X\text{–}H\cdots B \approx 180°$. Bond energy for this strong bond is $> 40\,\mathrm{kJ\,mol^{-1}}$. Because of the directional characteristic, it is concluded that in addition to the electrostatic interaction, there is also a covalent contribution to this bond. A strong hydrogen bond can be described as a resonance of the three canonical structures

$$\overset{\delta-}{:\underset{\cdot\cdot}{\ddot{\mathrm{X}}}}\!-\!\overset{\delta+}{\mathrm{H}}\cdots\overset{\delta-}{:\underset{\cdot\cdot}{\ddot{B}}}\!-\!\overset{\delta+}{A}\leftrightarrow :\underset{\cdot\cdot}{\ddot{\mathrm{X}}}:^{-}\cdots\mathrm{H}^{+}\cdots\overset{\delta-}{:\underset{\cdot\cdot}{\ddot{B}}}\!-\!\overset{\delta+}{A}\leftrightarrow :\underset{\cdot\cdot}{\ddot{\mathrm{X}}}:^{-}\cdots[\mathrm{H}-\underset{\cdot\cdot}{\ddot{B}}-A]^{+}$$

Weak hydrogen bonds are primarily electrostatic. There is a continuum with respect to most properties between the strongest of the hydrogen bonds which are rare, and those which normally exist in the various compounds, which are weak. In weak hydrogen bonds the bond lengths $H\cdots B > X\text{–}H$ and the bond angles $X\text{–}H\cdots B \approx 160 \pm 20°$. The weaker the hydrogen bond, the smaller are the associated directional characteristics. Bond energies for these weak bonds are $< 20\,\mathrm{kJ\,mol^{-1}}$.

In contrast to the carbonyl group, which shows a high affinity for protons and forms relatively strong hydrogen bonds with proton donors, the siloxane group has a very low affinity for protons and does not form stable hydrogen bonds. This cannot be explained in the light of electronegativity, because carbon is more electronegative than silicon (2·55 and 1·90, respectively) and consequently the Si–O group should be more polar. The VB description of the Si–O–Si group explains why this group serves as a weak proton acceptor. In this description the involvement of the non-bonding electrons in the π system reduces their ability to accept protons. Hydrogen bonds, if formed, would be very weak and primarily electrostatic. According to the VB description of the C=O group there is an sp^2 hybridization on the oxygen. One hybridized and one non-hybridized orbital overlap with similar orbitals of the carbon to form the double bond. The other two non-bonding hybridized orbitals can easily be involved in proton acceptance.

The VB description of the Si–O–Al group explains why this group serves as a stronger proton acceptor than the Si–O–Si group. According to this description there is an sp^2 hybridization on the oxygen. One hybridized and one non-hybridized (sp^2 and p) orbital overlap with hybridized and non-hybridized (sp^3 and d) orbitals of the silicon to form σ and π bonds. A second hybridized (sp^2) orbital of the oxygen overlaps with hybridized (sp^3) orbital of the aluminium to form a σ bond. The non-bonding hybridized (sp^2) orbital of the oxygen can easily be involved in proton acceptance.

We shall demonstrate how the Al for Si substitution contributes to the formation of hydrogen bonds between parallel layers of clay minerals.

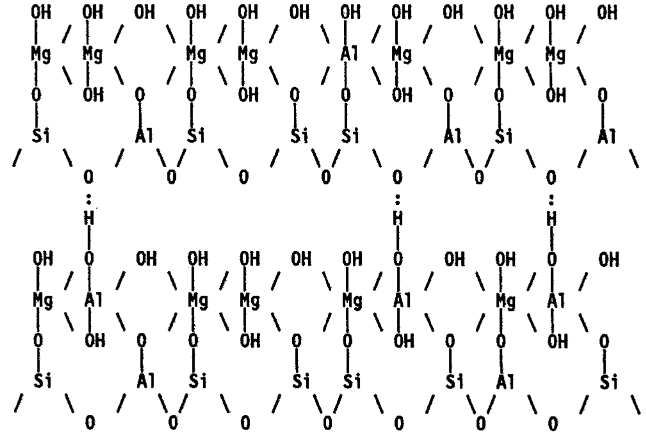
4.1. *Interlayer hydrogen bonds in serpentines*

The kaolin and serpentine minerals belong to the di and trioctahedral variety, respectively, with TO-type layers stacked one above the other in the c direction. As a result of the polarization of the Si–O and O–H bonds, the surface oxygen and proton planes become negatively and positively charged, respectively. Electrostatic attraction forces between planes of parallel layers with opposite charges (Giese 1973) and van der Waals interactions (Cruz *et al.* 1972) lead to the stacking of the TO layers one above the other. The inductive effect of Mg^{2+} on the polarization of the O–H bond is weaker than that of Al^{3+}, and consequently, the overall positive charge on the OH plane is lower in serpentines than that in kaolin. As well, the involvement of non-bonding electrons of oxygens of the O plane in serpentines in the π bond system of the Si is higher compared with that in kaolins, and, consequently, the overall negative charge on the O plane is lower in serpentines. Because of the lower charges of the OH and O planes, electrostatic-type attraction forces are weaker in serpentines compared with kaolins.

It is therefore expected that in serpentines the contribution of the van der Waals forces to the overall attraction between the layers, will be higher than that of the electrostatic forces. In most kaolin-type minerals the stacking of the layers results in crystals with parallel flat layers whereas in most serpentine type minerals the layers are not necessarily flat. For example, in chrysotile they are rolled up like a carpet (Yada 1971). In antigorite there is a periodical inversion in the direction of the $[SiO_4]$ tetrahedra, leading to a curled TO layer (Liebau 1985). This is associated with the high contribution of electrostatic attraction to the stacking in kaolin-type minerals and of van der Waals attraction to the stacking in serpentine minerals.

Isomorphous substitutions are rare in kaolinites. Only small amounts of iron can be truly integrated within the kaolinite structure. Serpentines, on the other hand, show very large isomorphous substitutions of many metallic cations for Mg in the octahedral sheet and Al for Si in the tetrahedral sheet (Faust and Fahey 1962).

Short-range pairing of O and OH groups of siloxanes and aluminols belonging to tetrahedral and octahedral sheets, respectively, of two parallel successive layers, results in interlayer hydrogen bonds in kaolinite. The O–H–O angles are 168, 146 and 144° (Adams 1983), indicating that these hydrogen bonds are very weak. The contribution of hydrogen bonds to the stacking of the kaolinite layers is thus very small. No interlayer hydrogen bonds are formed in serpentines because magnesols are poor proton donors compared with aluminols and, also, because of the very weak basic strength of the oxygen plane of the trioctahedral layer, compared with that of the dioctahedral layer. Substitution of trivalent ions in the tetrahedral and octahedral sheets increases the



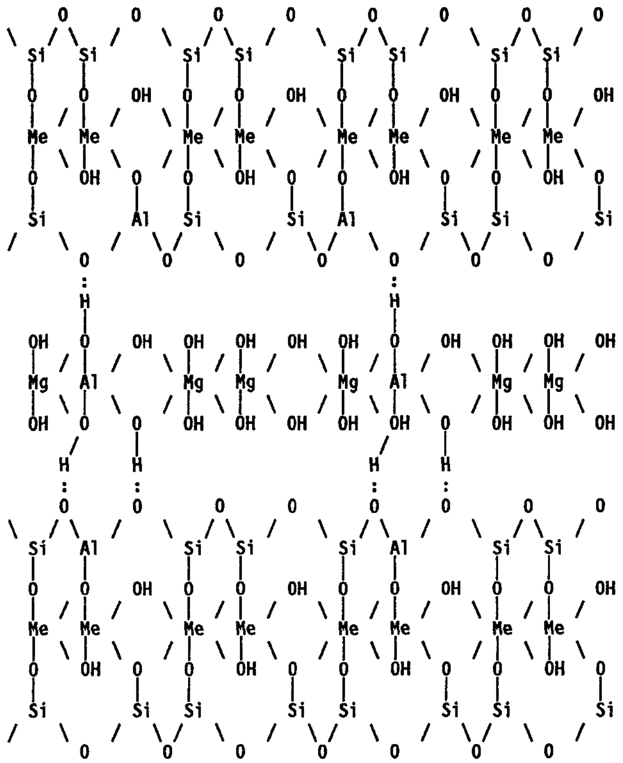
Scheme 5. Interlayer hydrogen bonds between Al–OH and Si–O–Al groups in serpentines with tetrahedral and octahedral substitutions, side view.

polarization of the oxygen and proton planes and the delocalization of some hydrogen atoms. In addition to the electrostatic and van der Waals types of interaction between the layers, the superposition of oxygen and hydroxyl planes of successive layers within a single serpentine crystal gives rise to pairing of O and OH groups belonging to substituted tetrahedral and octahedral sheets, respectively, which results in interlayer hydrogen bond formation (scheme 5, Heller-Kallai *et al.* 1975).

The existence of hydrogen bonds is well demonstrated by the appearance of a characteristic OH band at about 3400 cm^{-1}, in the infrared absorption spectrum of the mineral sample. This weak band appears in addition to the principal absorption at about 3700 cm^{-1}, which is characteristic for OH groups that are not involved in hydrogen bonds. The 3400 cm^{-1} band may be relatively sharp or very broad, corresponding to a range of frequencies. It is absent whenever there is no isomorphous substitution in the tetrahedral sheet. This band appeared when alkali halide disks were dried at 300°C and persisted up to 620°C, when dehydroxylation started. Similar hydrogen bonds are formed between two layers of amesite, a serpentine with the highest substitution of Al for Si (Serna *et al.* 1977*b*).

4.2. *Interlayer hydrogen bonds in chlorites*

An infrared absorption band in the 3400 to 3435 cm^{-1} region appears in the spectra of trioctahedral chlorites and septechlorites, in addition to the absorption at about 3600 cm^{-1} (e.g. Tuddenham and Lyon (1959), Hayashi and Oinuma (1967), Senkayi



Scheme 6. Interlayer hydrogen bonds between Al–OH and Si–O–Al groups in chlorites with tetrahedral substitution, side view.

et al. (1981)). The former absorption is characteristic for hydrogen bonded OH groups whereas the latter characterizes non-bonded OH groups. These minerals consist of TOT type layers, separated from each other by quasi-brucite sheets that are octahedral Mg hydroxides with replacements of Mg by Al and Fe, and consequently the sheets are positively charged. The TOT-type silicate layer is negatively charged as a result of tetrahedral substitution of Al for Si, and the deficiency of charge is balanced by an excess charge in the quasi-brucite sheet. The entire structure is neutral. The two parts of the structure are held together by electrostatic forces and by hydrogen bonds formed between the hydroxyls of the quasi-brucite sheet and oxygens of the TOT-type layers (scheme 6). Hydrogen bonds are formed when oxygens and hydroxyls belonging to substituted tetrahedra and octahedra, respectively, are paired.

5. The effect of tetrahedral substitution on the wettability of the silicate layer

5.1. *Wettability of talc, pyrophyllite and vermiculite*

Schrader and Yariv (1990) determined the surface characteristics of the perforated oxygen plane from hydration properties of pyrophyllite and talc. Advancing contact angles of water were compared to those of tetrabromoethane on freshly prepared surfaces of these minerals. The advancing contact angle of water on the randomly oriented particles is about 61° and on the crystals on tape backing which have a preponderance of cleavage plane orientation, the advancing angle is about 83°. The latter value seems to be the most representative of that of the cleavage plane. Both values are in the hydrophobic range. The water layer which is in contact with the clay has the hydrophobic hydration water structure. That is, water clusters are formed with intra-cluster hydrogen bonds. No hydrogen bonds are formed between water molecules and the oxygen plane.

The advancing contact angles of tetrabromoethane on tape supported samples (which expose a preponderance of cleavage plane surface) are about 44°. This value indicates that the cleavage surface is not strongly ‘organophilic’.

For comparison, advancing contact angles of water and of tetrabromoethane were measured on freshly prepared surfaces of vermiculite layers. The advancing contact angles of water ranged between 0 and 15°. These values are virtually, or completely, in the hydrophilic range (the non-zero contact angles are probably due to organic contamination from the air). Vermiculite has much tetrahedral substitution and hydrophilicity of this mineral may result from the presence of O atoms undergoing sp^2 hybridization, as expected for brittle mica. The water layer in contact with the clay has the hydrophilic hydration water structure, i.e., hydrogen bonds are formed between water molecules and the oxygen plane in the solid–liquid interface. Hydrophilicity may also result from exchangeable hydrated Mg^{2+} cations which are attached to the oxygen plane. However, when surface Mg^{2+} was exchanged by Li^+ or Cs^+, the latter being a water structure breaker, the advancing contact angles of water again ranged between 0 and 15°, indicating that the tetrahedral substitution is the principal cause of the hydrophilicity of vermiculite.

The advancing contact angles of tetrabromoethane ranged between 0 and 14°. This organophilicity of vermiculite is due either to a contribution of oxygen lone-pair donor electrons to the London dispersion forces, or possibly to tetrabromoethane acting as a Lewis acid on this donor pair.

Mulla *et al.* (1984) applied statistical mechanics and molecular dynamics simulations for describing the properties of vicinal water located between two parallel uncharged oxygen planes of pyrophyllite, separated by 3·3 nm. They concluded that the vicinal water differed substantially from bulk water in the static orientation of molecular dipole moments and the rate of relaxation of these moments. However, no significant differences between the radial distribution functions of interfacial and bulk water were observed from these simulations. Hydrogen bonding patterns and the rate of self-diffusion in the first two water layers near the silicate surfaces were significantly different from that in bulk water. This water should be regarded as a model for the 'hydrophobic hydration' water of the clay that will be mentioned in the next Section, in connection with the fine structure and acidity of the interlayer space of TOT minerals.

5.2. *The extent of the smectite–water interaction*

Smectites are expected to be more hydrophilic than talc or pyrophyllite, because of their electric charge. The advancing contact angles of water on hectorite (with no tetrahedral substitution) and montmorillonite (with a few tetrahedral substitutions) have recently been determined by the capillary rise method. They are 63 and 42·5°, respectively, the former being less hydrophilic (Costanzo, Giese and van Oss 1990, Giese, Costanzo and van Oss 1991). These values are lower than those of the hydrophobic talc or pyrophyllite but are very different from that of the hydrophilic vermiculite, whose charge originates mainly from tetrahedral substitution.

In aqueous suspensions of Na–smectites most dispersed particles are composed of single silicate layers. By comparing spectra of suspensions of Na–smectites with that of pure water, it is possible to specify the extent of the interfacial region whose spectroscopic properties are significantly perturbed by the clay–water interaction, relative to the spectrum of bulk water. The study of near i.r. spectra of Na–hectorite, with no tetrahedral substitution, showed that the H_2O spectrum is perturbed up to the adsorption of about two and a half water monolayers. Beyond about two and a half water monolayers the near i.r. spectroscopic properties of the adsorbed water are not perturbed significantly (Prost 1981).

The extent of the interfacial region in Na–hectorite was examined by nuclear magnetic resonance (NMR) study of the temperature dependence of the spin–lattice relaxation time, T_1, of the protons (Woessner 1980). It was estimated that this value for the adsorbed water molecules differs from the value for the molecules in bulk liquid water only in the first nanometer away from the clay surface which is equal to approximately three water monolayers.

These experimental results are in good agreement with the statistical mechanics and molecular dynamics simulations of Mulla *et al.* (1984) for describing the properties of vicinal water at the surface of pyrophyllite.

Infrared spectroscopic properties of Na–montmorillonite, with very small tetrahedral substitution, showed that perturbation of the water spectrum continues with adsorption beyond four water layers (Salle de Chou *et al.* 1980).

Observations on water structure in smectite–water systems were reviewed by Sposito and Prost (1982).

6. The effect of Al for Si substitution on the hydration and acidity of interlayer space of TOT minerals

The present Section deals with the contribution of the oxygen plane to the interlayer space of smectites and vermiculites. The interlayer space of a TOT clay mineral is the space between two parallel silicate layers, bordered by two oxygen planes. The interlayer is the principal space for adsorption of inorganic and organic ions and molecules.

Lahav and Bressler (1973) showed that the surface oxygen networks are changed with variations in the exchangeable cations and with their associated water of hydration. This can be explained in part by the penetration of the bare metallic cation into the ditrigonal hole and the interactions between this cation and the oxygens which form the ditrigonal hole. This interaction results in a rotation of the silica tetrahedra. When the metallic cation is hydrated the direct interaction between the bare metallic cation and the oxygen does not exist and the rotation angle of the silica tetrahedra is changed. This provides a partial explanation for the change in *b* dimension with water content observed by Ravina and Low (1972). During the hydration of a smectite mineral, a decrease of the concentration of non-hydrated cations decreases the force exerted by these cations on the oxygen plane and thereby decreases the tendency of the tetrahedra to rotate. Both the force exerted by the cations on the oxygen plane and the tendency of the tetrahedra to rotate increase as a result of tetrahedral substitution.

When smectites or vermiculites are in contact with vapour or liquid water they swell. Swelling is the process by which the clay mineral expands beyond the original *c* axis spacing $\approx 0{\cdot}95$ nm, as a result of the adsorption of water into the interlayer space. Water adsorption by swelling clay minerals has been described in terms of an initial crystalline phase and a later osmotic phase (Low and Deming 1953, Bolt and Miller 1955, Low 1961, Norrish 1972). The crystalline phase adsorption concerns the adsorption of the first few water monolayers on mineral surfaces driven by cation and surface hydration energies. The later adsorption has been termed 'osmotic' since it was considered to be controlled by chemical potential gradients between the adsorbed and free water. For this adsorption swelling pressure has been related to

(i) the difference in the concentration of ions in the interlayer and external solutions and
(ii) the difference in the potential energy of the water in these solutions.

The two stages will now be described in more detail.

6.1. *Crystalline adsorption and the fine-structure of interlayer water*

The structure of interlayer water is the result of superposed effects: on the one hand, the nature of the oxygen planes which border this space, and, on the other hand, the nature of the exchangeable cations located in this space, as follows.

(I) The nature of the oxygen plane depends on the charge of the silicate layer and on whether the charge results from tetrahedral or octahedral substitution. With no tetrahedral substitution the oxygen plane is composed predominantly of oxygen atoms belonging to siloxane groups that do not form stable hydrogen bonds with water molecules, and consequently the hydration of this surface is hydrophobic in nature. With tetrahedral substitution the oxygen plane is composed of oxygen atoms belonging to Si–O–Al groups that can form hydrogen bonds with water molecules, and consequently the hydration of this surface can to some extent be hydrophilic in nature.
(II) The exchangeable cation is surrounded by a 'hydrophilic hydration' cosphere in which the organization of water molecules differs from that in the remainder of the interlayer space (Fornes and Chaussidon 1975).

Water in the interlayer space cannot be treated as a bulk continuum. A simple model for interlayer water assumes the presence of three zones having differing water structures which may be distinguished in the interlayer space (Yariv and Cross 1979, chap. 7). Two zones contain ordered water, the water molecules comprising the hydration atmosphere of the ions and the solid–liquid boundary layer at the flat oxygen plane being distinguished as zones A_m and A_O, respectively (the subscripts m or O signify hydration of exchangeable metallic cation or oxygen plane, respectively). A third zone, B_{Om}, is a disordered zone separating the ordered zones A_O and A_m. In zone A_O the clay–water interface exerts an ordering influence on the water structure, reducing the thermal amplitudes of the intermolecular vibrations and consequently reducing the density of the water layers in the immediate neighbourhood of the clay surface. In zone A_m the dipolar axis of each water molecule passes through the ion centre. The strong polarizing field of the exchangeable cation attenuates the molecular motion of water in this zone. Zone B_{Om} is subjected to the competing demands of water structures associated with zones A_m and A_O. These two influences counteract each other and water in this fault zone has no structure.

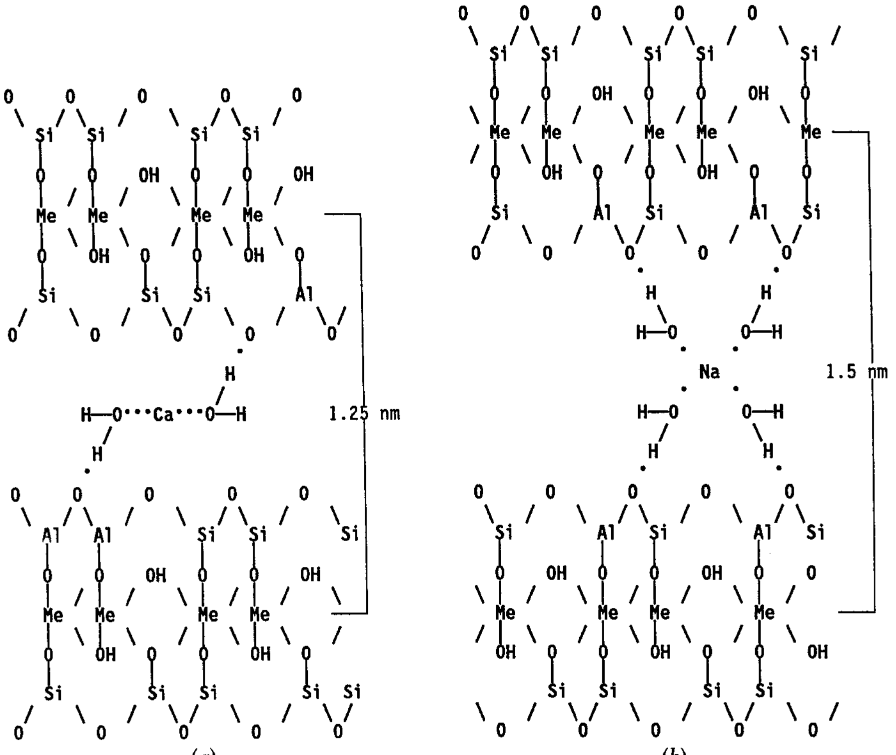
6.1.1. *Zone* A_m

This zone comprises the hydration sphere of exchangeable cations, water molecules reacting as bases and cations as Lewis acids. The size of zone A_m decreases with increasing ionic size and increases with increasing ionic charge. For example, at a very low relative humidity Ca^{2+} or Mg^{2+} smectites form hexahydrates whereas Li^+ or Na^+ smectites form planar trihydrates. Under similar conditions zone A_m does not exist around exchangeable Cs^+ because of its low electric charge and large size. In the trihydrates the water molecules form a triangle and the cation is located in its centre. A single water layer is obtained in the interlayer with a spacing of about 1·25 nm (scheme 7 (*a*)). In the hexahydrates the water molecules form an octahedron and the cation is located in its centre. A bilayer of water is obtained in the interlayer with a spacing of about 1·5 nm (scheme 7 (*b*)).

Similar structures for zone A_m were observed whether the central cations were alkali or whether they were alkaline-earth metal cations (Prost 1975).

Water molecules which form the hydration shells of the exchangeable cations are more acidic than molecules of bulk water and may serve as proton donors. This is the consequence of the electric repulsion induced by the central cation on the H of the coordinating water molecule. In the case of vermiculites or smectites with tetrahedral substitutions, the coordinating water molecules may form hydrogen bonds with atoms of the oxygen plane at siloxane sites where Si has been replaced by Al (Yariv and Heller 1970, Farmer and Russell 1971, Suquet *et al.* 1977, Schrader and Yariv 1990).

De la Calle *et al.* (1975) have shown by X-ray techniques that in Na–vermiculite the stacking of layers is accomplished without rotations of the layers which form the tactoid. This corresponds to an ordered state with the ditrigonal cavities of two adjacent layers facing each other. This ordered organization of layers is the consequence of hydrogen bonds which are formed between the water molecules of the hydration shell and O atoms of the oxygen plane. Three water molecules in the upper face of the hydration octahedron and three water molecules in its base donate protons to oxygens which form the ditrigonal holes in the oxygen planes of the clay (scheme 7). The Na^+ is located in the centre of the hydration octahedron, between parallel ditrigonal cavities.



(*a*) (*b*)

Scheme 7. The hydration of an exchangeable cation in the interlayer space of a swelling clay mineral (smectites or vermiculite), side view. In the case of tetrahedral substitution hydrogen bonds are formed with clay surface oxygen atoms at sites where Si has been replaced by Al. (*a*) trihydrate, water mono-layer and (*b*) hexahydrate, water bilayer (De la Calle *et al.* 1975, Prost 1975, Suquet *et al.* 1977).

6.1.2. *Zone* A_O

The presence of a solute interface, such as the smectite surface, imposes restriction on the rotation of adjacent water molecules, thereby forming a boundary in the wave motion of clustered water molecules. Thus, the solute forces the positioning of nodes in the spatial arrangement of wave units in the liquid state. Such a two-dimensional node may readily form at the clay–water interface, because the hexagonal array of atoms in the oxygen plane was a high degree of compatibility with the structure of ice. The water molecules form an extended plane within the liquid. A layer of solvent 3–4 nm thick would spread itself parallel to the surface, next to it, extending over macroscopic distances in two dimensions. In the tactoid, the layer-shaped hydration cluster is sandwiched between each pair of silicate layers. One should remember that the sandwiched water layer occurs quite readily, not requiring any special energetic mechanism for its creation, because clusters form in the solvent alone. To conclude, the hydration layers are naturally occurring water clusters but their arrangement and final macroscopic form is determined by the clay. The two participants, clay and water, together build the superstructure (Watterson 1989).

The structure of zone A_O depends on the degree of hydrophilicity of the oxygen plane. At a hydrophobic oxygen plane of, for example, hectorite, hydrophobic water clusters are obtained, forming zone A_O. The OH groups of the water molecules are not necessarily directed toward the hydrophobic surface siloxane-type oxygens, and the organization of the water molecules is such that they are closely linked to one another by hydrogen bonds. To understand why this hydrophobic water region is formed, one should consider the interlayer space as a cage wherein the thermal amplitude of the water molecules is reduced. When the water molecules enter into this cage they undergo a loss in entropy, while at the same time a new structure is formed. In this case water⟨– –⟩oxygen plane interactions are weak, the extent of water⟨– –⟩water interactions is enhanced and water clusters, which form zone A_O, become large.

In the case of laponite, which is a synthetic hectorite, molar heat of dehydration of untreated clay (41·61 kJ mol^{-1}) is very similar to the molar heat of vaporization of water (44·02 kJ mol^{-1} (Greenwood and Earnshaw 1984)), probably due to the fact that water clusters in the interlayer space of untreated laponite are similar to water clusters in liquid water (Yariv *et al.* 1992).

With increasing extent of tetrahedral substitution, as in the case of vermiculite, the hydrophilic character of the oxygen plane increases and the extent of water⟨– –⟩oxygen plane interactions is enhanced. In this system water⟨– –⟩water interactions are weaker than water⟨– –⟩oxygen plane interactions and, consequently, water clusters which form zone A_O are small. The size of water clusters also decreases with increasing charge density of the silicate layer. This is due to the fact that an increase in the charge density of the surface is associated with increasing concentration of co-ions. The latter serve as cluster breakers.

For montmorillonite saturated with sodium, Mamy (1968) has suggested that the monolayer hydrate consists of tetrahedral distribution of water molecules arranged in a strained hexagonal icelike configuration, with intermolecular bonds formed between neighbouring water molecules and between water molecules and oxygen atoms in the silicate surface. Because of very few tetrahedral substitutions in montmorillonite, some of the water molecules have a hydroxyl group proton inside a ditrigonal cavity of the silicate surface, and the net of the intracluster hydrogen bonds among the adsorbed water molecules is broken in places. A similar hydrophobic structure occurs with other monovalent montmorillonites. For the one layer hydrate of montmorillonite saturated with bivalent cations, the same structure may not exist because of the strong solvation of the exchangeable cations.

The molar heat of dehydration of untreated montmorillonite (27·42 kJ mol^{-1}) is less than the molar heat of vaporization of water and also is less than the molar heat of dehydration of untreated laponite, probably due to the fact that water clusters in the interlayer of untreated montmorillonite are smaller than water clusters in liquid water or in laponite (Yariv *et al.* 1992).

Hydrophilic hydration of zone A_O may occur in vermiculite and in smectites with charge originating from tetrahedral substitution. Walker (1956) and Fripiat and Stone (1978) described different stages of hydration of Mg–vermiculite. We shall use their description to demonstrate the presence of zone A_O even with a very low water coverage as a result of hydrogen bond formation. In a fully hydrated Mg–vermiculite each water sheet is arranged in a regular hexagonal pattern and the interlayer cations are located midway between water monolayers in octahedral coordination. At this stage there are more than 12 water molecules per Mg^{2+}. Zone A_m is composed of the Mg hexahydrate. The rest of the water comprises zone A_O. Zone B_{Om} does not exist in this case because zone A_O forms a direct extension of zone A_m. The c axis spacing at this stage is 1·481 nm. From this spacing the HOH–O distance (where O is an oxygen atom belonging to the oxygen plane) was calculated as 0·31 nm.

On partial dehydration a contraction of the *c* axis spacing to 1·436 nm occurs. The interlayer water network consists of two monolayers arranged in a distorted hexagonal pattern. At this stage there may be between 9 and 12 water molecules per Mg^{2+}. Zone A_m is again composed of the Mg hexahydrate but zone A_O, which is composed of the remaining water, is not fully developed. The HOH–O distance for this dehydration stage was calculated as 0·29 nm. The *c* axis spacing of the fully hydrated sample is determined by the fully developed zone A_O and the HOH–O distance is characteristic for water of that zone. On the other hand, the *c* axis spacing of the partly dehydrated sample is determined by zone A_m and the HOH–O distance is characteristic for water of that zone. The shorter HOH–O distance in the latter stage is an indication of stronger hydrogen bonds. Water in zone A_m is more acidic compared to water in zone A_O, forming stronger hydrogen bonds with atoms of the oxygen plane.

Upon further dehydration the *c* axis spacing decreases to 1·159 nm. A similar spacing is obtained for water content ranging between three and eight molecules per Mg^{2+}. At this stage a single water monolayer is present in the interlayer. With water content of less than three molecules per Mg^{2+}, the *c* axis spacing becomes smaller. There is a marked difference between the hydrophilic arrangement of H_2O molecules in the 1·159 nm phase and the hydrophobic arrangement shown for Na–montmorillonite, where the tetrahedral arrangement of the water structure is maintained. The monolayer hydrate consists of hexagonal distribution of water molecules. Zone A_m consists of hydration shells of three water molecules. The metallic cation being located above and/or below the centre of the ditrigonal hole of the oxygen plane. Zone A_O is composed of all the remaining water molecules.

6.1.3. *Zone* B_{Om}

Being non-clustered, water molecules of zone B_{Om} reveal a dual activity. They act simultaneously as proton donors as well as proton acceptors. The size and properties of zone B_{Om} depend on the polarizing power of the exchangeable cation. The greater this power is, the more acidic is the associated hydration shell (zone A_m), the greater is the disturbance on zone A_O and consequently, the greater is the extension of zone B_{Om}. For example, zone B_{Om} forms a great fraction of interlayer water in Al montmorillonite in which every discrete zone A_m extends over a large volume. However, since the total number of Al ions in the interlayer is only one third of the number of monovalent ions, the total volume occupied by A_m is comparatively small, leaving a considerable fraction of the interlayer for adsorption of water through the formation of zones B_{Om} and A_O. Al–montmorillonite has sites of a high basic strength together with sites of a high acid strength. This peculiar property results from the high activity of water molecules in zone B_{Om} (Yariv *et al.* 1969).

The extent of water structure breaking increases with the size of the cation in its non-hydrated state, and consequently the size of zone B_{Om} increases concomitantly. For example, Cs–montmorillonite shows basic and acidic properties as a result of the presence of this zone. Due to its large size Cs^+ breaks the hydrophobic structure of zone A_O. Being very large and having a small electric charge, this exchangeable cation imparts only a small polarizing effect which is not sufficient to form zone A_m. Conversely, with decrease in ion size, zone B_{Om} contracts and may disappear, as with exchangeable Li^+ in smectites. In this system the cations are accommodated within the clusters of water A_O.

6.2. *Osmotic adsorption and water structures in clay suspensions*

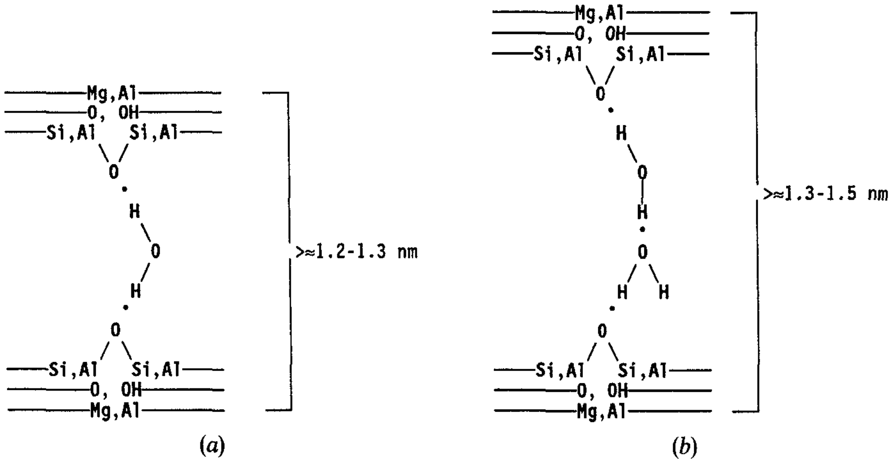
When the formation of two or three monolayers of water is completed, osmotic adsorption leads to further swelling of the interlayer space. Adsorbed water is actually a solution with a high concentration of counterions, whereas free water is the bulk solution. The adsorbed water molecules form clusters in the interlayer. The relationship between several inorganic exchangeable ions and the degree of swelling of vermiculites and smectites was examined by several investigators (Quirk 1968 *a*, *b*, Suquet, de la Calle and Pezerat 1975, Low and Margheim 1979, Low 1980, 1987, Heller-Kallai and Yariv 1981). Montmorillonite saturated with the small alkali ions Li^+ and Na^+, to some extent also K^+, exhibits extensive swelling. Of all alkali saturated vermiculites, only the Li clay exhibits extensive swelling. On the other hand, saturation with bivalent ions, such as Ca^{2+}, Mg^{2+}, Ni^{2+}, Zn^{2+}, or Cd^{2+}, restricts swelling of vermiculite to a *c* axis spacing of 1·40–1·50 nm and of montmorillonite to 1·90–2·00 nm. Swelling of Cs montmorillonite or vermiculite gives rise to a *c* axis spacing of only 1·20 nm. The behaviour of beidellite and saponite, the two smectites with tetrahedral substitution, is similar to that of vermiculite.

In a highly swollen clay there are grossly expanded phases with *c* axis spacings equivalent to more than 4 nm in which the interlayer water must be much more liquid-like away from the silicate surfaces, showing some similarities to aqueous salt solutions rather than to crystalline hydrates. Like liquid phase water, the 'osmotic' adsorbed phase consists of clusters, the size and nature of which depend on the silicate layer and on the ions present in the system. In aqueous salt solutions the zone which consists of clusters similar to those of pure liquid water is named zone *C*, whereas the zone which consists of the hydrated ions is named zone *A*. Similarly we shall assign the zone consisting of clusters similar to those of bulk water, by the term C_c.

The effect of exchangeable cations on the swelling properties of the expanding clay mineral can be attributed to the presence of the different water zones. Water molecules of zone A_m are proton donors, and may form hydrogen bonds with oxygen planes of TOT clay minerals. Thus, the hydrated exchangeable cations may bridge between two parallel silicate layers by forming stable hydrogen bonds with the oxygen plane (scheme 7). This bridging process limits the swelling of TOT clays to a *c* axis spacing of 1·4–1·5 nm.

Whereas these hydrogen bonds, which are characteristic for water molecules of zone A_m, restrict the swelling of the clay above a certain limit, the presence of zones A_O or C_c does not necessarily limit osmotic swelling to any degree. Li and Na ions do not break the water structure of zones A_O or C_c of montmorillonite and hectorite, since, because of their small sizes, these ions can fit into the interstitial cavities of the water structure. In beidellite, saponite and vermiculite, due to the tetrahedral substitution and hydrophilic hydration of the oxygen plane, water clusters of zones A_O or C_c are probably smaller than those of bulk water. Only Li ions do not break the water structures of zones A_O and C_c, whereas the larger Na ions do break the A_O structure, and thus restrict swelling and penetration of C_c clusters into the interlayer space. The intense ionic fields of multivalent cations cause local destruction of the water structure of this region and the formation of zone A_m.

Water in zone B_{Om} is the major water fraction in Cs–montmorillonite, Cs–vermiculite and in K–vermiculite. Being non-structured, individual water molecules in zone B_{Om} may form water bridges between two parallel oxygen planes, as shown in scheme 8 (*a*), and thereby restrict swelling of K or Cs–montmorillonite and vermiculite to a *c* axis spacing of 1·20 nm.



Scheme 8. A single water molecule (*a*) and two molecules (*b*) of zone B_{0m} forming a bridge between two parallel TOT silicate layers, side view. The interactions between the bridging water molecules and each of the oxygen planes are localized hydrogen bonds.

Organic aliphatic ammonium cations restrict swelling of the montmorillonite to 1·3–1·5 nm. In general, introduction of organic matter into clay interlayers renders them hydrophobic. Thus montmorillonite saturated with organic ammonium ions does not show expansion on exposure to water. The explanation for this phenomenon can be as follows. The positive charge density of the organic ion is too small to cause hydrophilic hydration corresponding to zone A_m. The large size of the organic ion, on the other hand, leads to disruption of the hydrophobic hydration structure A_0. Water penetrating into the interlayers is therefore non-structured (zone B_{0m}) and may form water bridges between adjacent oxygen planes, thus preventing swelling. Organic ammonium cations resemble Cs^+ in this respect (Heller-Kallai and Yariv 1981; Yariv *et al.* 1992). Depending on the size of the organic cation, which is larger than that of Cs^+, a *c* axis spacing larger than 1·2 nm is required to accommodate most organic cations. A spacing of 1·3–1·5 nm allows the formation of very small non-structured water clusters bridging between adjacent oxygen planes, as shown in scheme 8 (*b*). Since this water is more active than water of zone A_m, this type of bridging occurs also in clays with no or with slight tetrahedral substitution. For example, the spacing of tributylammonium–laponite (a synthetic hectorite) ranges between 1·35 and 1·6 nm (Yariv *et al.* 1992).

Hydrogen bonds are responsible for this type of bridging or that in which water molecules of zone A_m are involved, and thereby are responsible for limitation in the swelling process of TOT clays. It is therefore obvious that the degree of swelling will decrease with the strength and number of hydrogen bonds. Consequently, from all TOT clays, the interlayer of hectorite is the most expandable and that of montmorillonite is more easily expanded than that of saponite or vermiculite and more hydrophobic water can be adsorbed.

6.3. *Acidic and basic properties of the interlayer space*

In the present Section we describe the mutual interactions between the oxygen plane and the acid sites. These interactions determine the bulk and fine properties of the interlayer space.

Water of zone A_m dissociates under the polarizing effect of the metallic cation as follows

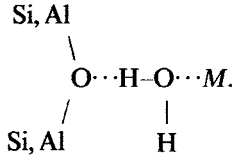
$$[M(OH_2)_x]^{m+} \rightarrow [M(OH)(OH_2)_{x-1}]^{(m-1)+} + H^+.$$

A similar polarizing effect of cations occurs in aqueous salt solutions leading to an increased number of hydrogen bonds between water molecules and extension of the ordered self-atmosphere zone of hydrated ions. This ordered zone increases with increasing polarizing power of the soluble ions. Because of steric hindrance in the interlayer space, zone A_m cannot extend as much as the hydration self-atmosphere zone of ions in liquid water and is therefore a stronger proton donor. Moreover, the water structure in the interlayer space contains more lattice vacancies than normal water, and the dielectric constant of this water is less than that of liquid water. Consequently, interlayer protons are more mobile than in liquid. According to Touillaux *et al.* (1968) the degree of dissociation of interlayer water is 10^7 times higher than that in the liquid. The proton donating tendency increases as the water content of the interlayer space decreases.

The polarization of the interlayer water is affected by the nature of the exchangeable cation. Greater polarizing ability of the interlayer cations increases both the strength and number of acid sites per surface unit area. Acid strength of hydrates of some common ions decreases in the following sequence: Al, Fe, Mg, Ca, Li, Na, K and Cs. Mortland and Raman (1968) showed that the degree of protonation of sorbed ammonia depended upon the hydrolysis constant of the interlayer hydrate and that the degree of protonation may be regarded as a measure of the acidity of the interlayer space. In base saturated smectites and vermiculites, ammonia molecules form hydrates such as $M^{m+}\text{–}OH_2\cdots NH_3$, via hydrogen bonds or accept protons originating from water dissociation, forming hydroxy complexes $[M\text{–}OH]^{(m-1)+}$ and NH_4^+. In Al–montmorillonite NH_3 reacts with protons to form ammonium ion.

Frenkel (1974) studied surface acidity of homo-ionic montmorillonites by titrating the clay with amines in the presence of coloured indicators. He confirmed the observation on the polarization of the interlayer water by the exchangeable cations and the effect of charge and size of the cation on its polarizing ability, but demonstrated that some of the very high acidity values reported in the literature are due to artifacts at measurement.

The acid strength of water of region A_m depends on whether the charge of the clay mineral originates from tetrahedral or octahedral substitution. Oxygen planes of layers, where in the charge originates from the tetrahedral substitution, form strong hydrogen bonds with polarized water molecules having the following structure:



In this structure the water molecule forms a bridge between the exchangeable cation and the oxygen plane. As a result of this hydrogen bond formation, the ability of the bridging water molecule to donate its second proton to any acceptor is diminished, indicating that the acid strength is weak.

From nuclear magnetic resonance studies on Li hectorite, in which the charge originates from octahedral substitution, Conard (1976) suggested that the trihydrated

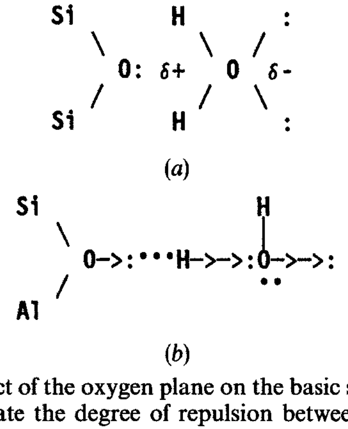
Li cation is fixed above the six oxygens of the hexagonal cavity by delocalized bonds. The absence of any localized hydrogen bonding between the water-H and the oxygen plane, accounts for the high acidic properties of that clay. Protonation of an adsorbed base by this water molecule is therefore more readily affected with octahedrally charged than with tetrahedrally charged clay minerals (Yariv and Heller 1970; Farmer and Russell 1971, Suquet *et al.* 1977).

Water molecules in zone B_{Om}, not being structured, are more active than water molecules in structured zones A_O or A_m. They may interact with negative charge sites on the oxygen planes. Some water molecules will be oriented with the positive ends of the dipoles towards the oxygen planes, thus imparting a basic character to interlayer water (scheme 9 (*a*)). Some water molecules will react as proton donors imparting an acid character to interlayer water. In most cases 'acidic' water predominates over 'basic' water and obscures the presence of the latter (Yariv and Shoval 1982).

In clays with tetrahedral substitution non-structured water molecules form hydrogen bonds with O atoms of the oxygen plane. As a result of this proton donation, the basic strength of the water molecule increases.

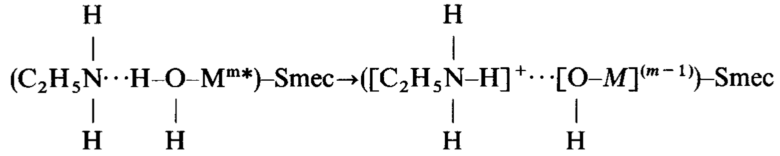
The increase of basic strength of the hydrogen bonded water molecules can be explained by the inductive effect model. The lone pair electrons on the O atom of the Si–O–Al group, which is involved in the formation of the hydrogen bond, induces an electric effect of repulsion on the non-bonding electron pair of the water-O and the latter may act as an electron pair donor, thus becoming a basic site (scheme 9 (*b*)). The size of zone B_{Om} and the strength of the hydrogen bond between the water molecule and the oxygen plane increase with the polarizing power of the metallic cation. Consequently the number and strength of basic sites of this type, increase with increasing polarizing power of the exchangeable cations. The behaviour of interlayer water as proton acceptors was observed mainly in the presence of exchangeable Al or Fe and less in the presence of mono and divalent cations (Yariv *et al.* 1969, Yariv and Shoval 1982).

The exchangeable metallic cations and the hydration state of the clay play a major role in the adsorption of organic polar molecules. Strong bases are protonated during adsorption, yielding positive ions. The extent of this reaction depends on the basic



Scheme 9. The inductive effect of the oxygen plane on the basic strength of an adsorbed water molecule. Arrows indicate the degree of repulsion between bonding and non-bonding electron pairs. (*a*) With no tetrahedral substitution there is no inductive effect on the non-bonding electrons of the water O. (*b*) With a tetrahedral substitution of Si by Al, a strong hydrogen bond is obtained and the lone pair electons of the oxygen plane O, which is involved in the hydrogen bond, induces an electric repulsion on the non-bonding electrons of the water O.

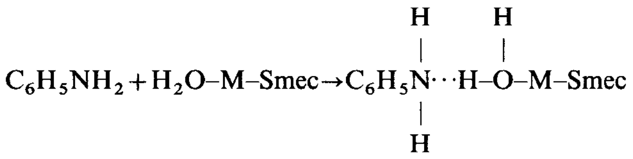
strength of the organic compound and the polarizing power of the metallic cation. For example, adsorbed aliphatic amine is protonated in the interlayer space as follows:



$$(C_2H_5\overset{H}{\underset{H}{N}}\cdots H\text{–}\underset{H}{O}\text{–}M^{m*})\text{–Smec}\rightarrow([C_2H_5\overset{H}{\underset{H}{N}}\text{–}H]^{+}\cdots[\underset{H}{O}\text{–}M]^{(m-1)})\text{–Smec}$$

(Bodenheimer *et al.* 1966, Yariv and Heller 1970, Heller-Kallai *et al.* 1972). Water coordinated to the exchangeable cation serves as proton donor.

With decreasing basic strength of the organic compound and/or decreasing polarizing power of the exchangeable metallic cation, associations are obtained via hydrogen bondings, wherein a water molecule acts as a proton donor. This can be illustrated by the adsorption of aromatic amines which are weak bases, such as aniline:



$$C_6H_5NH_2+H_2O\text{–}M\text{–Smec}\rightarrow C_6H_5\overset{H}{\underset{H}{N}}\cdots H\text{–}\overset{H}{O}\text{–}M\text{–Smec}$$

(Yariv *et al.* 1968, 1969; Heller and Yariv 1969).

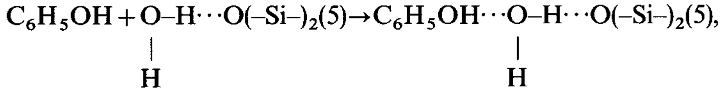
In this adsorption reaction the nitrogen atom serves as the nucleophilic site. If the adsorbed molecules are proton donors they may react with two different basic sites:

(i) the oxygen plane and
(ii) negative poles of water molecules of zone B_{Om}, hydrogen bonded to the oxygen plane.

This is shown by the sorption of indoles, phenols or fatty acids:

$$C_8H_6N\text{–}H+O(\text{–Si–})_2(5)\rightarrow C_8H_6N\text{–}H\cdots O(\text{–Si–})_2(5),$$

and



$$C_6H_5OH+\underset{H}{O}\text{–}H\cdots O(\text{–Si–})_2(5)\rightarrow C_6H_5OH\cdots\underset{H}{O}\text{–}H\cdots O(\text{–Si–})_2(5),$$

$$C_nH_{2n+1}COOH+O(H_2)\cdot Al\cdot O(\text{–Si–})_2\rightarrow C_nH_{2n+1}COOH\cdot\cdot O(H_2)\cdot Al\cdot O(\text{–Si–})_2,$$

(Sofer *et al.* 1969, Saltzman and Yariv 1975, Yariv and Shoval 1982).

7. π interactions between aromatic compounds and the oxgyen plane of TOT clay minerals with Al for Si tetrahedral substitution

7.1. *Adsorption of aromatic cationic dyes*

Most aromatic cationic dyes are metachromic, that is, their visible absorption spectra change with their concentrations. In dilute aqueous solutions monomeric species are present and are characterized by band α. In more concentrated aqueous solutions dimeric species are present and are characterized by a blue shifted band (band β) which is further shifted towards the u.v. region with concentration. The electronic absorptions result from π→π* transitions and the blue shifts are indications for π interactions between parallel species in the dimers and polymers. Thus, dye aggregation is caused by the interactions between π electrons of parallel aromatic rings of the dye cations.

In addition to the blue shift of this transition, a red shift is also observed, indicating the formation of hydrogen bonds between proton donor components in the system and the dye cation. Both shifts are observed when the cationic dyes are adsorbed by the clay minerals. However, in the present review article we shall discuss only those blue shifts which are associated with the tetrahedral substitutions.

The adsorption reactions of aromatic cationic dyes by clay minerals take place mainly by the mechanism of 'long-range' cation exchange reactions. In many cases it is accompanied by metachromasy, which is an indication for π interaction in which the dye cation is involved. In the case of minerals such as montmorillonite and vermiculite, metachromasy appears immediately after the adsorption of trace amounts of the dye. From electronic spectroscopy study supplemented by X ray and thermal analysis, it was concluded that this adsorption is accompanied by a 'short-range' π bonding between the aromatic entity and the oxygen plane of the silicate layer (Yariv and Lurie 1971). This type of interaction occurs only with tetrahedrally substituted clays, where some atoms of the oxygen plane serve as electron pair donors. This interaction involves the overlapping of non-bonding hybridized orbitals of O atoms, each with a lone pair of electrons, with the anti-bonding orbitals of the aromatic π systems. For this overlapping to occur, the aromatic ring must lie parallel to the oxygen plane (Cohen and Yariv 1984, Grauer *et al.* 1987a, Yariv *et al.* 1989a, b, Dobrogowska *et al.* 1991).

In laponite, a synthetic hectorite, on the other hand, metachromasy is observed only when the degree of saturation of the clay by the dye is equal to its cation exchange capacity. At this stage the clay is saturated, the particles lose their electric charge and the system flocculates. With smaller amounts of dye, the negatively charged particles are peptized and metachromasy is not observed. With amounts of dye greater than the cation exchange capacity, the particles gain positive charge and repeptize. Again the system does not show metachromasy. It was concluded that metachromasy in laponite systems stems from association of adsorbed dyes, in the interparticle space of flocs and consequently it is obtained only at the stage when the clay flocculates and does not occur when the clay is peptized (Yariv *et al.* 1989a, b, 1990).

Metachromasy in montmorillonite was recently reviewed (Yariv 1988). Absorption maxima of cationic dyes, such as pararosaniline, crystal violet, ethyl violet, malachite green, thionin, methylene blue and pyronin Y show significant blue shifts from band α to band β of approximately 50 nm in spectra of dyes adsorbed on montmorillonite, relative to their spectra in aqueous solutions. Spectra of adsorbed safranin, acridine orange and Janus green showed smaller shifts, of approximately 15–20 nm, whereas those of adsorbed rhodamine B and rhodamine 6G did not show any blue shift.

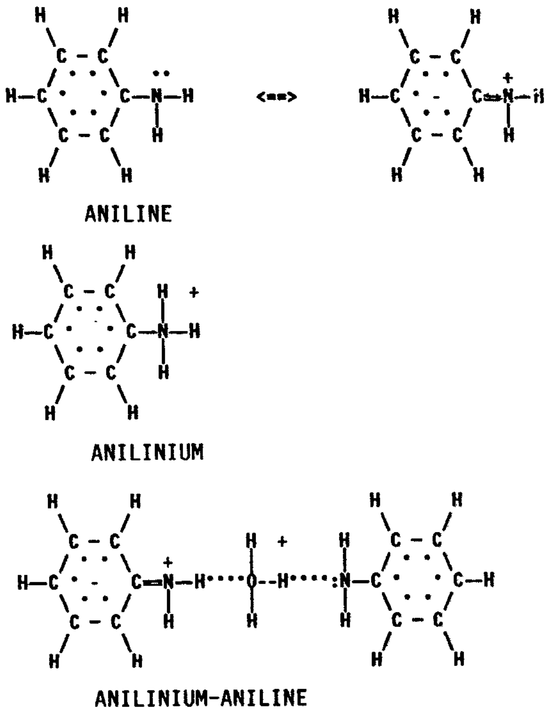
Rhodamine B and rhodamine 6G consist of xanthene moiety and a phenyl ring perpendicular to the three xanthene rings. These two dyes are only weakly metachromic in aqueous solutions, due to steric hindrance. However, due to this hindrance, they do not show metachromasy at all when adsorbed on clays. Since the phenyl ring is sterically constrained to be roughly perpendicular to the planar xanthene group, this cannot approach the oxygen plane sufficiently to permit π interaction (Grauer *et al.* 1984, 1987*b*).

7.2. *The orientation of adsorbed aromatic cations in montmorillonite*

Pyridinium montmorillonite has a basal spacing of 1·26 nm (Farmer and Mortland 1966). A similar basal spacing (1·26–1·29 nm) was observed with montmorillonite treated with anilinium or small derivatives of this aromatic cation (Heller and Yariv 1970). According to Greene-Kelly (1955) a 1·26 nm spacing requires an arrangement of the aniline or pyridine cation having planes parallel to the silicate surface. This was confirmed for pyridine by pleochroic i.r. study (Farmer and Mortland 1966). As more aniline or pyridine is adsorbed by the ammonium montmorillonite, an ammonium–amine complex is formed in the interlayer space and the orientation changes abruptly from horizontal to a nearly vertical one. The *c* axis spacing at this stage is between 1·47 and 1·60 nm.

The difference between the *c* axis spacings of ammonium–montmorillonite, on one hand, and amine saturated montmorillonite or ammonium–amine clay, on the other, can be attributed to the location of negative charge in the aromatic ring. In the anilinium or pyridinium cation the nitrogen is positively charged and does not take part in the conjugated double-bond system. Consequently the aromatic entity has no excess of electrons and no charge and is not repelled by the negatively charged oxygen plane. In the aniline or pyridine molecule the nitrogen does take part in the conjugated double-bond system by donating its lone pair of non-bonding electrons. The aromatic entity becomes negatively charged and is repelled by the oxygen plane. The orientation of the aromatic ring changes from horizontal to a nearly vertical one. In the ammonium–amine the positive charge is located on the hydronium ion which bridges between the two amine molecules and the charge on the aromatic ring is also negative (scheme 10).

It is probable that the horizontal orientation of the aromatic ammonium cations in the interlayer space is governed by the π interactions between the aromatic entity and

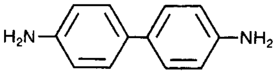


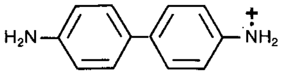
Scheme 10. Electric charge distribution over aniline, anilinium (cation) and anilinium–aniline. (·) electrons in π system.

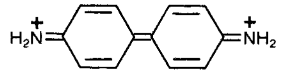
the oxygen plane of the montmorillonite layer. π interactions are obtained as long as the aromatic ring is not negatively charged, i.e. as long as the anti-bonding π orbitals are empty. When the aromatic system has an excess of electrons, the anti-bonding π electrons repel the lone pair electrons of the oxygen and the π interaction is not obtained.

7.3. *Stabilization of aromatic radicals in the interlayer space of montmorillonite*

Some simple colourless aromatic molecules convert to their coloured derivatives when they are brought into contact with clay minerals. A well known example of this type of reaction is the coloration of smectites by benzidine (I) (Lahav and Raziel 1971). The colourless neutral molecule benzidine is converted by oxidation to its blue derivative, monovalent semiquinone (II), and by further oxidation to the yellow derivative, divalent quinone (III).


(I)


(II)


(III)

Benzidine blue is a radical and like most radicals, it is not stable. When formed in aqueous solution in the absence of clays, e.g. by the enzyme peroxidase, it is converted into benzidine yellow in a few seconds. In contrast, benzidine blue obtained in the presence of montmorillonite, is very stable and may persist for several months. This is probably due to stabilization by π interactions between the oxygen planes of the clay and the positive radicals (Yariv *et al.* 1976).

8. Conclusions

In the present review we demonstrated that the basic strength of the oxygen plane of clay minerals is increased with the tetrahedral substitution of Si by Al. Weak acids react with the oxygen plane, accepting electron pairs or donating protons. Hydrogen bonds are formed between oxygens and hydroxyls in substituted serpentines and chlorites. We also showed that tetrahedral substitution of Si by Al makes the oxygen plane hydrophilic. Smectite minerals differ one from the other by their swelling properties. Water molecules form strong hydrogen bonds with the oxygen plane of clays with tetrahedral substitution. Consequently, the swelling of smectites and vermiculites with charge located at the tetrahedral sheets is prevented to some degree. Aromatic cations form π bonds with oxygens of clays with tetrahedral substitution.

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