

## INFLUENCE OF SILICA CONTENT ON THE SURFACE CHARGE CHARACTERISTICS OF ALLOPHANIC CLAYS

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**Abstract**—The surface and charge characteristics of 6 allophanic clays originating from a climatosequence of Andisols have been studied by titration, ion retention, surface area, and reactivity measurements. Several properties of these clays, such as the pH of zero charge, the magnitude of the surface area, and the reactivity of structural hydroxyl groups, appear to be governed by their chemical composition, especially by their silica content. A similar relationship between the above properties and silica content also exists for synthetic aluminosilicate gels (often quoted in the literature as possible models of allophanes), despite their different structure to the natural clays. An explanation is that as desilication proceeds, octahedral polymeric units of aluminum progressively individualize in both the synthetic and natural samples. The surface areas of the allophanic clays, based on the slope of the titration curve at pH 7, are closely related to the amounts of structural hydroxyl that can react with fluoride at about the same pH. The permanent negative charges are always very low, even for silica-rich, allophane-bearing samples. It is therefore suggested that all of these clays should be virtually free of tetrahedral aluminum.

**Key Words**—Allophane, Andisols, Desilication, Soils, Specific surface, Zero point of charge.

### INTRODUCTION

In 1972, Van Raij and Peech characterized the surface charge of highly weathered soils. Since then, the literature has confirmed the validity of their methods and concepts not only for sesquioxide rich Oxisols and Ultisols (Keng and Uehara, 1973; Morais *et al.*, 1976; Gallez *et al.*, 1976; Gillman and Bell, 1976), but also for Andisols (El Swaify and Sayegh, 1975; Basulabramanian and Kanehiro, 1978) and for Spodosols (Laverdière and Weaver, 1977; Hendershot *et al.*, 1979). Because the sign and magnitude of the surface charge of the above soils is so dependant on several solution parameters (i.e., concentration and type of electrolytes, pH), it is meaningless to quote the surface charge characteristics of such constant potential colloids unless the precise experimental conditions and techniques for their determination are also given.

The possible relationship between the nature of superficial charge and certain soil-forming processes was described by Herbillon (1974). He emphasised the importance of desilication as a process capable of modifying the soil's surface properties because the presence of silica always renders the system more negative (regardless of whether the silica forms an integral part of the structure of the soil colloids or whether it is chemically adsorbed onto their surface).

The present study evaluates the effect of desilication on the surface properties of colloids originating from a

sequence of Andisols from Teneriffe (Canary Islands, Spain). A comparison is made of charge and surface characteristics between the natural short-range ordered clays described in this study and the aluminosilicate gels often presented as their models in the literature (e.g., Cloos *et al.*, 1969; Van Reeuwijk and de Villiers, 1970; Fey and Le Roux, 1976b; Perrott, 1977).

### SAMPLES

The location, genesis and properties of the sampled soils were discussed by Tejedor Salguero (1974), Tejedor Salguero *et al.* (1978), and Quantin *et al.* (1978). It should be noted that on the northern slopes of Teneriffe, the combination of climate, time, and topography produces volcanic ash soils showing different stages of weathering. Table 1 gives the chemical and mineralogical composition of the samples examined in this study as well as the classification of the soils from which they came using standard Soil Taxonomy criteria (Soil Survey Staff, 1975).

The clays from these Andisols are characterized by an abundance of short-range ordered aluminosilicates such as allophane and imogolite. The silica content of the clays from more highly weathered samples decreased whilst, simultaneously, some crystalline iron and aluminum oxides and hydroxide were segregated, with one exception. The exception is the clay "Las Lajas" which came from a soil that, according to Quantin *et al.* (1978), exhibits no textural, structural, or consistency properties characteristic of an Andisol. Its clay fraction also consists principally of halloysite(10Å). The last sample mentioned in Table 1 is a clay (Akaka) from the subsurface horizon of a "Typic Hydrandept" from Hawaii. The charge characteristics of a similar

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Table 1. Origin and chemical and mineralogical characteristics of selected Andisols, Tenerife, Spain.

Soil series and horizon	Classification (soil)	R <sup>3+</sup> / (R <sup>3+</sup> + Si) (clay)	Al <sup>3+</sup> / (Al <sup>3+</sup> + Si) (clay)	Clay mineralogy	
				Dominant phases	Minor phases
Chio, B/C	Typic Vitrandept	0.45	0.36	Allophane	Halloysite
Aguamansa II, B <sub>2</sub>	Typic Dystrandept	0.55	0.44	Allophane	
Aguamansa I, B/C	Typic Dystrandept	0.62	0.53	Allophane	
Dos Cupressos, B	Typic Dystrandept	0.65	0.59	Imogolite > allophane	Gibbsite, goethite
Las Aves, B/C	Typic Dystrandept	0.72	0.65	Allophane > imogolite	Gibbsite, goethite
Las Lajas, B	Andic Haplumbrept	n.d.	n.d.	Halloysite	Gibbsite, goethite
Akaka (Hawaii), 64–114 cm	Typic Hydrandept	0.77	0.61	Allophane, gibbsite, goethite <sup>1</sup>	

<sup>1</sup> See also El Swaify and Sayegh (1975).

Akaka soil have also been studied by El Swaify and Sayegh (1975) and Basulabramian and Kanehiro (1978).

Clay size fractions (<2 μm) were obtained from the lower B or B/C horizons of the soils given in Table 1 using mild pretreatments to avoid irreversible modification of the colloid surfaces. The soils (<2 mm) were ultrasonified in distilled water at pH 8–9 (adjusted using 0.1 N NH<sub>4</sub>OH) and the resultant suspensions transferred into Atterberg cylinders. After sedimentation, the <2-μm fraction was siphoned off, flocculated using 0.1 N HCl, and centrifuged. The solid was dried at ≤50°C under an infrared lamp and then mildly hand-ground. Unless mentioned, all determinations relate to the weight of sample dried at 105°C overnight.

## METHODS

### Potentiometric titrations

The procedure used followed closely that of Van Raij and Peech (1972). Serial titration curves were made using an individual clay sample for each point. To a 50-mg sample in a 50-ml beaker, appropriate amounts of NaCl, 0.1 N HCl or 0.1 NaOH, and water were added to give a final volume of 20 ml. The final concentration in NaCl varied from  $1 \times 10^{-3}$  N to 1 N. The beakers were kept at 20°C (±0.5°C) in an atmosphere of argon and water vapor to prevent carbonation and evaporation. After three days, the pH (VTW 398 pH meter with an Ingold 2223 microelectrode) was read. The amount of H<sup>+</sup> and OH<sup>-</sup> adsorbed by the clay was taken as equal to the amount of acid and base added minus the amount needed to bring a similar volume of NaCl solution (at the same concentration as the sample) to the pH of the sample suspension.

### Ion-exchange capacities

Schofield's procedure for ion-exchange capacity (1949) as modified by Fey and Le Roux (1976a) was used. Clays were equilibrated in a 0.05 N KCl solution (Wada and Harada, 1969) and brought to different pH values by adding either HCl or KOH. For two samples, pairs of cation-exchange and anion-exchange capacities were determined in the presence of 0.5 N KCl. The

amount of K<sup>+</sup> remaining in the solution was determined by flame photometry, while Cl<sup>-</sup> was measured by potentiometry.

### Surface area measurements

Specific surface areas were determined by two procedures. In the first, the amount of ethylene glycol monoethyl ether (EGME) retained by the clay as a monolayer was determined gravimetrically (Heilman *et al.*, 1965). The second, based on a paper by Pyman and Posner (1978), used the slope of the titration curve at pH 7 determined in the presence of 1 N NaCl as an indifferent electrolyte.

The surface area was estimated from  $S_0 = 1.14T$ , where  $S_0$  is the specific surface area expressed in m<sup>2</sup>/g, T is the slope (μeq/g × pH) of the titration curve at pH 7 in presence of a high concentration of an indifferent electrolyte (here, 1 N NaCl), and 1.14 is an empirical constant due to the calibration of the technique against "amorphous" oxides of known surface areas.

### Reactivity with respect to F<sup>-</sup>

The procedure used was that of Bracewell *et al.* (1970), as modified by Perrott *et al.* (1976). Twenty-five milligrams of clay was added to 5 ml of a 0.85 M NaF solution at pH 6.8. The OH<sup>-</sup> "exchanged" against F<sup>-</sup> was titrated during a period of 25 min, and the resultant value (expressed in meq/100 g) was taken as the reactivity index (R<sub>F</sub>).

### Sample analysis

The chemical analyses of Si, Al, and Fe were performed after alkaline fusion of the samples. Silica was determined gravimetrically, and Al and Fe by atomic absorption. From these analyses the atomic ratios R<sup>3+</sup>/(R<sup>3+</sup> + Si) (with R<sup>3+</sup> = Al<sup>3+</sup> + Fe<sup>3+</sup>) and Al<sup>3+</sup>/(Al<sup>3+</sup> + Si) were computed (Table 1). The mineralogical composition of the samples was estimated by visual inspection of their X-ray powder diffraction diagrams. The electron microscope was used to estimate the relative contents of allophane and imogolite and to confirm the presence of minute amounts of tubular halloy-

site in one sample (Chio). The results of these determinations are also reported in Table 1.

## DEFINITIONS

The charge characterization approach adopted in this paper is similar in many respects to those given in previous papers (see Introduction section). So that the precise meaning of the symbols used here is clear, the parameter notations will be summarized. Most of these agree with the paper of Gillman and Uehara (1980) (see also Uehara and Gillman (1980) for a review of the theoretical background of these notations).

**ZPT.** ZPT (zero point of titration) is the pH of the clay suspension when no base or acid is added.

**pH<sub>0</sub>.** pH<sub>0</sub> is the pH for which the net charge resulting from the adsorption of H<sup>+</sup> and OH<sup>-</sup> ions is zero. pH<sub>0</sub> is measured by the intersection point of titration curves performed in the presence of varying concentrations of indifferent electrolytes.

**ZPNC.** ZPNC (zero point of net charge) is the pH for which the net surface charge is zero. At the ZPNC, the cation-exchange capacity (CEC) is equal to the anion-exchange capacity (AEC). For systems free of permanent charges, ZPNC should coincide with pH<sub>0</sub>. For mixed systems where permanent and nonpermanent charges coexist, ZPNC may differ from pH<sub>0</sub>. In such systems, the position of ZPNC is also expected to vary with the concentration and type of electrolyte used to measure the CEC and AEC.

**σ<sub>p1</sub>.** σ<sub>p1</sub> (first estimate of the permanent charge = σ<sub>p</sub> in Gillman and Uehara, 1980) is the charge (negative or positive) determined by the difference between AEC and CEC when these values are taken at pH<sub>0</sub>. If ZPNC = pH<sub>0</sub>, σ<sub>p1</sub> is equal to zero. If, however, ZPNC ≠ pH<sub>0</sub>, the theory of mixed systems predicts that σ<sub>p1</sub> should be estimated when the CEC and AEC values are measured in the presence of very low concentrations of electrolytes (Uehara and Gillman, 1980). In the present study:

$$\sigma_{p1} = \text{AEC}_{\text{pH}_0} - \text{CEC}_{\text{pH}_0}$$

in the presence of 0.05 N KCl.

**σ<sub>p2</sub>.** σ<sub>p2</sub> (second estimate of the permanent charge) is measured by the amount of H<sup>+</sup> necessary to bring the system from ZPT to pH<sub>0</sub>. Van Raij and Peech (1972) and Espinoza *et al.* (1975) considered that whenever ZPC > pH<sub>0</sub>, the added H<sup>+</sup> first exchanged against cations occupying permanent negative sites. This interpretation, however, was not accepted by Gillman and Uehara (1980).

## RESULTS

### Charge characteristics

Figure 1 shows the titration curves obtained with the samples listed in Table 1. It can be seen that the param-

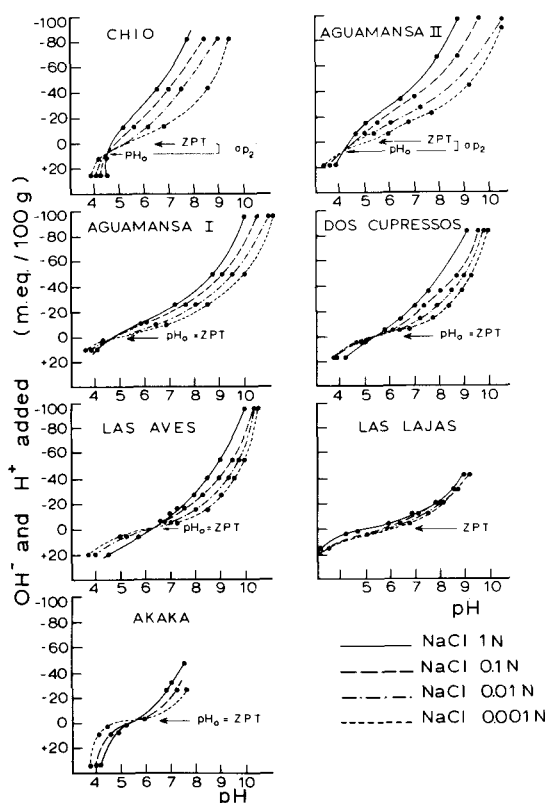


Figure 1. Adsorption density (meq/100 g) of H<sup>+</sup> and OH<sup>-</sup> as influenced by NaCl concentration.

eters ZPT, pH<sub>0</sub>, and σ<sub>p2</sub>, can be readily extracted from these curves. The values of these parameters have been listed in Table 2.

Figure 2 illustrates the variation with pH of CEC and AEC determined in the presence of 0.05 N KCl and, for samples "Aguamansa II" and "Las Aves," in the presence of 0.5 N KCl. The ZPNC position (in 0.05 N KCl) was obtained by extrapolation of the experimental data for the Chio and Aguamansa II samples and by interpolation for the others. From Figure 2 the AECs and CECs at pH<sub>0</sub> can also be estimated. The above data, together with computed σ<sub>p1</sub> value, are listed in Table 2.

Figures 1 and 2 illustrate the variable charge characteristics shown by all the colloids. The Las Lajas sample appears to be exceptional in that its AEC is low and little affected by variation in pH (Figure 2), whereas its titration curves (Figure 1) fail to reveal any pH<sub>0</sub> (at least not above pH 3). These observations indicate that the Las Lajas soil, which is distinct from the other Andisols of the sequence on the basis of several morphological properties, also consists of colloids that behave differently in the presence of potential determining ions. This is in good agreement with the observation that halloysite is an important constituent of the clay of this soil (Table 1).

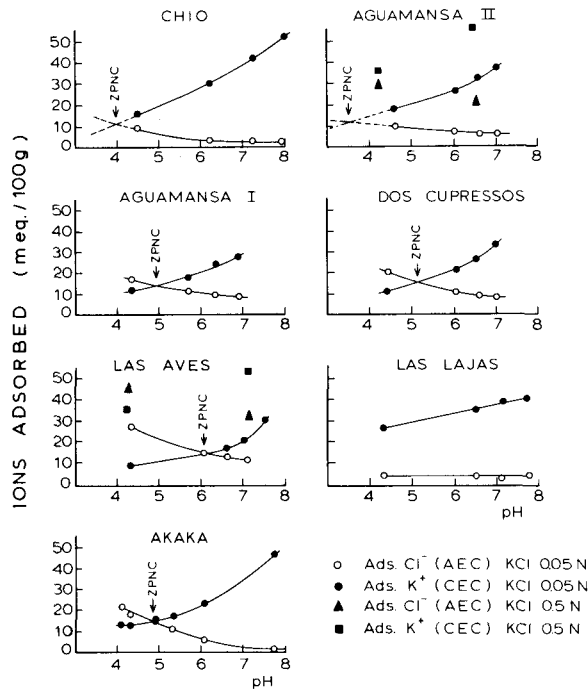


Figure 2. Influence of pH and KCl concentration on CEC and AEC.

Omitting the Las Lajas sample, the data in Table 2 show that a decrease in the silica content is related to an increase in  $pH_0$  and ZPNC, a common tendency for both the synthetic aluminosilicate gels and the allophanic clays. As a further comparison between the natural and synthetic systems, Figure 3 gives the ZPNC values (obtained in the presence of 0.1 N NaCl) of the five synthetic Al-Si mixed gels studied by Perrott (1977) indicated as a solid line curve. As noted by Pyman (1978), this curve is representative of synthetic systems. Further, the results that are given in, or that can be inferred from, several different studies (e.g., Mattson, 1928; Van Reeuwijk and de Villiers, 1970; Herbillon, 1974; Fey and Le Roux, 1976a) all follow the same trend as depicted by the curve shown in Figure 3. For

synthetic compounds, therefore, it is well documented that the evolution of ZPNC (or of any parameter having approximately the same meaning, such as  $pH_0$ ), with chemical composition does not exactly follow the theoretical dependence derived from the model of Parks (1967) and illustrated by Perrott (1977) (dotted line on Figure 3). Specifically, for Al/(Al + Si) ratios from about 0.4 to 0.6 (i.e., in the composition range of many natural samples), the relationship between ZPNC and composition is poorly predicted by Parks' model.

The additional data in Figure 3 refers to natural allophanic clays examined either in the present study (Table 2) or in previous publications. Despite the polymineralic nature of several of these samples and their possible contamination with organic colloids, their zero charge parameter (ZPNC or  $pH_0$  or both) shows an evolution strikingly similar to that of pure synthetic gels. This shows that the variation of charge characteristics with composition is similar for both synthetic and natural poorly organized Si-Al colloids.

Table 2 also shows that the two clays richest in silica (Chio and Aguamansa II) are not only characterized by the lowest  $pH_0$  but also by a permanent negative charge whose magnitude could be estimated using either the  $\sigma_{p1}$  or the  $\sigma_{p2}$  approach. For the other samples, with the exception of the Akaka clay, ZPT is equal to  $pH_0$  so that their  $\sigma_{p2}$  is zero, whereas their  $\sigma_{p1}$  can be either slightly negative or even positive. In agreement with the observations by Basulabramanian and Kanehiro (1978) concerning a soil sample of the same origin, the Akaka clay examined in the present study exhibits a large difference between its  $pH_0$  and its ZPNC. Moreover, its measured  $\sigma_{p1}$  is the highest of the present samples. El Swaify and Sayegh (1975) reported that the soils belonging to the Akaka series might contain some adsorbed sulfate whose presence could affect their charge characteristics. To test this possibility, the clay was equilibrated with either KCl or  $K_2HPO_4 + KCl$  solutions. The sulfate test was negative with the KCl but positive with the  $K_2HPO_4 + KCl$  solution. Evidently, the high  $\sigma_{p1}$  recorded for the Akaka clay may be due to the inability of  $Cl^-$  anions to compete with sulfates which are specifically adsorbed on the surface.

Table 2. Charge characteristics compared to chemical composition.

Sample	$R^{3+}/(R^{3+} + Si)$	$Al^{3+}/(Al^{3+} + Si)$	$pH_0$	ZPNC	AEC at $pH_0$ (meq/100 g)	CEC at $pH_0$ (meq/100 g)	$\sigma_{p1}$ at $pH_0$ (meq/100 g)	$\sigma_{p2}$ (meq/100 g)
Chio	0.45	0.36	4.50	3.90 <sup>1</sup>	10	14	-4	-6
Aguamansa II	0.55	0.44	4.25	3.50 <sup>1</sup>	10	16.5	-6.5	-5
Aguamansa I	0.62	0.53	4.75	4.90	15.5	14	+1.5	0
Dos Cupressos	0.65	0.59	5.50	5.20	14	17.5	-3.5	0
Las Aves	0.72	0.65	6.30	6.10	14	15.5	-1.5	0
Las Lajas	n.d.	n.d.	<3	<4	n.d.	n.d.	n.d.	n.d.
Akaka	0.77	0.61	5.70	4.70	7	19.5	-12.5	0

<sup>1</sup> By extrapolation.



Consequently, in the absence of sulfates, the divergence between ZPNC and  $\text{pH}_0$  values would have been reduced and the inferred  $\sigma_{\text{p1}}$  would have been smaller.

The above example shows that, in agreement with the theoretical consideration of Uehara and Gillman (1980), the term "permanent charge" for the  $\sigma_{\text{p1}}$  value is inadequate if specific anionic adsorption occurs. However, other observations indicate that, even in absence of specific adsorption, both  $\sigma_{\text{p1}}$  and  $\sigma_{\text{p2}}$  values must be considered with caution. Both parameters depend on how closely the  $\text{pH}_0$  can be associated with a true isoelectric point. It is notable that whenever a significant  $\sigma_{\text{p2}}$  value can be measured (Table 2 and also Espinoza *et al.*, 1975), the  $\text{pH}_0$  is near or less than pH 4.5. In this range of pH, the clay minerals, especially the poorly organized ones, become soluble. Consequently, the  $\text{pH}_0$  is measured in solutions where  $\text{H}^+$  and  $\text{OH}^-$  are not the only potential determining ions and therefore equating  $\text{pH}_0$  to a genuine isoelectric point may no longer be justified.

#### Surface area and reactivity characteristics

Figure 2 shows that in the range of pH where these short-range ordered aluminosilicates are reasonably stable (pH 4.5 to 8), AEC-CEC plots fail to reveal any negative adsorption of either  $\text{K}^+$  (at low pH) or  $\text{Cl}^-$  (at high pH). Schofield's (1947) negative adsorption method to evaluate surface area (as suggested by Gillman and Uehara (1980) for constant potential clays) cannot therefore be used for allophanic clays. Perrott (1977) was also reluctant to use this approach noticing a slight negative adsorption of anions above pH 8 with some of his samples.

The results of surface area determinations based on the gravimetric determination of EGME ( $S_0\text{EGME}$ ) and on the slope of the titration curve at pH 7 ( $S_{0\text{T}}$ ) are listed in Table 3. The agreement between the two series of data is rather poor even though, for both series, the measured surface area decreases when the samples show evidence of crystalline oxide segregation. Moreover, the  $S_{0\text{T}}$  values appear to be systematically smaller than the  $S_0\text{EGME}$  values. In a comparative study by Aomine and Otsuka (1968) devoted to the characterization of the surface area of allophanic clays, the EGME method appeared to be the most favorable. More recently, reports have pointed out the microporous character of such clays (Rousseaux and Warkentin, 1976; Paterson, 1977; Wada and Wada, 1977). Pyman and Posner (1978) showed that, for similar synthetic microporous systems, the EGME procedure generally overestimates the true surface area. They argued that a correct estimation of surface area of such microporous compounds would be a value between that of the external surface area (based on the BET treatment of the  $\text{N}_2$  adsorption isotherm) and that obtained by the same treatment of the water adsorption isotherm. In their study,  $S_{0\text{T}}$  value, though completely

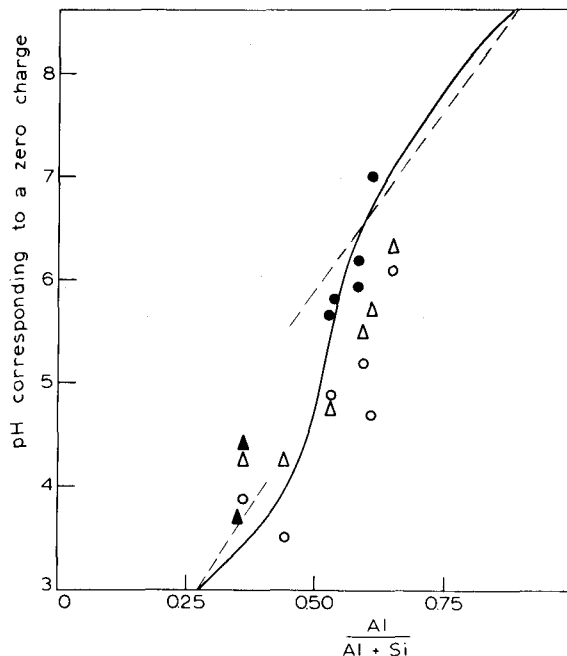


Figure 3. Effect of chemical composition on the location of the parameter measuring the point of zero charge. Solid line = ZPNC of synthetic gels (Perrott, 1977);  $\Delta$  =  $\text{pH}_0$  of natural clays (this study),  $\circ$  = ZPNC of natural clays (this study),  $\blacktriangle$  =  $\text{pH}_0$  of natural clays (Espinoza *et al.*, 1975),  $\bullet$  = ZPNC of natural clays (Fey and Le Roux, 1976a, 1976b; Perrott, 1977; Wada, 1977). The dotted line is the theoretical dependence derived from Parks' model by Perrott (1977).

empirical, appears to be a reasonable estimate of this "correct" value.

In the present study, no data were available to assess the validity of the conclusions by Pyman and Posner (1978), when applied to natural clays. However, it was of interest to evaluate the relationships between surface area as measured by two different procedures and the reactivity of the structural hydroxyls in presence of fluoride. The results of the reactivity test ( $R_F$ ) are listed in Table 3, and a plot of  $R_F$  against the two series of  $S_0$  values is given in Figure 4. The  $R_F$  data (Table 3) are in good quantitative agreement with those of Perrott *et al.*

Table 3. Surface area and reactivity values compared to chemical composition.

Sample	$\text{Al}^{3+}/(\text{Al}^{3+} + \text{Si})$	$S_0\text{EGME}$ ( $\text{m}^2/\text{g}$ )	$S_{0\text{T}}^1$ ( $\text{m}^2/\text{g}$ )	$R_F$ (mmole/100 g)
Chio	0.36	383	251	1227
Aguamansa II	0.44	549	228	1108
Aguamansa I	0.53	522	137	871
Dos Cupressos	0.59	420	194	920
Las Aves	0.65	342	125	654
Las Lajas	n.d.	247	68	82

<sup>1</sup>  $S_{0\text{T}} = S_0$  by titration.

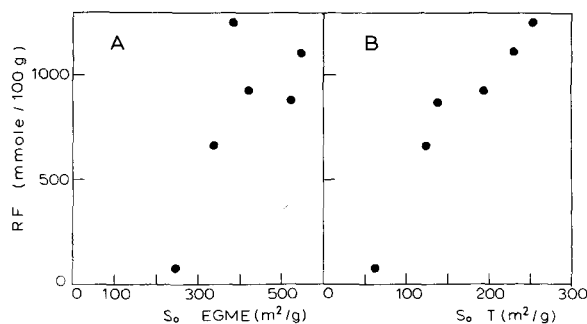


Figure 4. Plots of the fluoride reactivity index ( $R_F$  in mmole/100 g) against specific surface areas by EGME ( $S_{0EGME}$ ) and titration ( $S_{0T}$ ) methods.

(1976), if the samples consist essentially of allophanes (Chio and Aguamansa II) or halloysite (Las Lajas). The highest  $R_F$  value recorded here, however, appears to be two to three times smaller than those considered by Parfitt and Henmi (1980) as characteristic for "proto-imogolite" allophanes. Similar to the trend shown by the synthetic samples examined by Bracewell *et al.* (1970), the present  $R_F$  values also decrease as the silica content of the colloids decreases.

Figure 4 illustrates that  $S_{0T}$ , rather than  $S_{0EGME}$ , gives a better prediction of the reactivity and accessibility of OH structural groups of clays. Figure 4B indicates that there is a direct relationship between  $S_{0T}$  (i.e., the number of OH groups by unit weight that can dissociate between pH 6.5 and 7.5 in 1 N NaCl) and the total number of these groups able to "exchange" against  $F^-$  at approximately the same pH value. The ratio between these two values approximates to 1:50, if the better crystallized Las Lajas sample is omitted.

#### GENERAL DISCUSSION

In his review on the structure and properties of allophanes and imogolites, Wada (1977) questioned the usefulness of models based on synthetic aluminosilicate gels to understand and predict the behavior of these clays in soils. If considering structure, there is no doubt that Wada's conclusions are correct. Further, the major structural differences between the natural and synthetic Al-Si short-range ordered compounds are clearly demonstrated by imogolite (Cradwick *et al.*, 1972), a common transient stage of allophanic clays that are undergoing desilication. Indeed, the basic structural unit of imogolite is not a tetrahedral and condensed Si-Al network neutralized by positively charged aluminum hydroxypolymers (as in the structure proposed by Cloos *et al.* (1969) for a synthetic gel of similar composition). Rather it is a distorted octahedral aluminum sheet to which isolated orthosilicate anions are attached. In other words, the individualization of polymeric hydroxy-aluminum units in natural clays does not

take place in a manner strictly parallel to that observed in synthetic gels.

Although they differ structurally, a sequence of allophanic clays of varying chemical composition can still be compared to their synthetic counterparts in one respect at least. This is the progressive individualization of octahedral polymeric units and, finally, the segregation of free alumina phases as the silica content in both systems decreases. The observations reported here indicate that the net effect of this progressive alumina individualization on some fundamental surface and charge properties appears to be similar for both systems because the degree of desilication determines: (1) the point of zero charge and thus the sign of the charge developed at a given pH, and (2) the accessibility and reactivity of structural and superficial hydroxyl groups and thus the magnitude of the charge variation with the solution parameters.

It has also been shown that the magnitude of permanent negative charge present in allophanic clays, though small and difficult to measure accurately, seems to be influenced by the chemical composition of the clay. Qualitatively, this agrees with Henmi and Wada (1976) who noticed that the silica-rich allophanes showed a tendency to have more tetrahedral Al than allophanes rich in aluminum. Quantitatively, however, there remains a very large discrepancy between the theoretical permanent charge that could be computed from the content in tetrahedral Al and that determined experimentally. Two different types of explanation may be offered to explain this discrepancy. One could consider, like Fey and Le Roux (1976a), that the procedure used here to obtain the AEC and CEC values is inadequate to provide a good resolution of the charges actually present due to mutual neutralization of positive and negative charges in such systems. On the other hand, if most allophanes are based on a proto-imogolite framework as are those investigated by Parfitt and Henmi (1980) and Parfitt *et al.* (1980), then their tetrahedral Al content would be greatly reduced. In this latter case, the magnitude of the structurally related permanent charge would be in good agreement with that found here and in other similar studies.

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**Резюме**—Характеристики поверхности и заряда шести аллофановых глин, присходящих из климатического ряда Андисоли, исследовались путем титрования, измерений сохранения ионов, площади поверхности и реактивности. Несколько свойств этих глин, как рН нулевого заряда, величина площади поверхности, и реактивность структурных гидроксильных групп, регулируется химическим составом, особенно содержанием кремнезема. Похожая связь между этими свойствами и содержанием кремнезема наблюдалась также в случае синтетических алюмосиликатовых гелей (часто цитированных в литературе как возможные модели аллофанов), несмотря на различные структуры гелей и натуральных глин. Это объясняется тем, что в меру десихликации полимерические октаэдрические элементы алюминия придают более индивидуальный характер в обоих, натуральных и синтетических, образцах. Площади поверхности аллофановых глин, полученные на основе наклона кривых титрования при рН = 7, тесно связаны с количеством структурных гидроксильных групп, которые могут реагировать с фторидом при том же самом рН. Постоянные отрицательные заряды всегда очень низкие, даже в случае кремнеземо-богатых аллофановых образцов. В связи с этим предлагается, что все эти глины являются фактически свободны от тетраэдрического алюминия. [Е.С.]

**Resümee**—Die Oberflächen- und Ladungscharakteristika von 6 Allophanartigen Tonen, die von einer klimatischen Abfolge von Andisolen stammten, wurden mittels Titration, Ionenretention, Oberflächenbestimmung, und Reaktivitätsmessungen untersucht. Einige Eigenschaften dieser Tone, wie z.B. der pH-Wert bei Null-Ladung, die Größe der Oberfläche und die Reaktivität struktureller OH-Gruppen scheinen durch die chemische Zusammensetzung, vor allem vom SiO<sub>2</sub>-Gehalt, bestimmt zu werden. Eine ähnliche Beziehung zwischen den oben genannten Eigenschaften und dem SiO<sub>2</sub>-Gehalt ist auch bei synthetischen Alumosilikat-Gelen vorhanden (die in der Literatur oft als mögliches Modell für Allophane herangezogen werden) trotz ihrer zu natürlichen Tonen verschiedenen Struktur. Eine Erklärungsmöglichkeit ist, daß mit fortschreitender SiO<sub>2</sub>-Abnahme oktaedrische polymere Einheiten von Aluminium in zunehmendem Maße einzeln auftreten sowohl in den synthetischen als auch in den natürlichen Proben. Die Oberflächen der Allophan-artigen Tone (gewonnen aus der Neigung der Titrationskurve bei pH 7) hängt eng mit den Gehalten an strukturellen Hydroxyl zusammen, das mit Fluorid bei etwa dem gleichen pH reagieren kann. Die permanenten negativen Ladungen sind immer sehr niedrig, selbst für SiO<sub>2</sub>-reiche Allophan-haltige Proben. Es wird daher angenommen, daß alle diese Tone nahezu frei von tetraedrischem Aluminium sein sollten. [U.W.]

**Résumé**—Les propriétés de surface et de charge de 6 argiles en provenance d'une climatoséquence de sols à caractères andiques ont été étudiées en mettant en oeuvre des techniques telles que titrations potentiométriques, rétentions d'ions, déterminations de la surface spécifique, et tests de réactivité en présence de fluorure. Plusieurs caractéristiques de ces argiles comme la localisation du pH correspondant à une charge nulle, la grandeur de l'aire de surface, et la réactivité des groupements hydroxyliques structuraux sont déterminés par leur composition chimique, tout particulièrement par leur teneur en silice. De ce point de vue, on observe une remarquable analogie entre ces argiles naturelles et les gels aluminosiliciques synthétiques souvent présentés comme modèles d'allophanes dans littérature. Il est suggéré que, tant dans les échantillons naturels que synthétiques, la désilicification en entraînant l'individualisation progressive d'unités polymériques d'aluminium octaédrique est responsable des modifications observées. Pour les échantillons naturels, l'aire de la surface estimée par la pente de la courbe de titration à pH 7 montre une étroite relation avec la quantité d'hydroxyles structuraux réagissant avec l'anion fluorure au même pH. La charge négative permanente de ces argiles est toujours très faible, même lorsque leur teneur en silice est élevée. Ceci suggère que leur contenu en Al tétraédrique est négligeable.