SPANISH INVESTIGATIONS ON CLAY MINERALS AND RELATED MINERALS

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ABSTRACT

The studies undertaken by the Instituto de Edafología y Fisiología Vegetal on clay minerals and related silicates can be classified into three main groups: (A) Mineralogical identification and crystalline structure: (B) physico-chemical behavior; and (C) technical applications. They are summarized briefly.

MINERALOGICAL IDENTIFICATION AND CRYSTALLINE STRUCTURE OF SILICATES

In this field of study the task of the Institute has been centered on two problems: (1) Identification of the silicates of several Spanish deposits, and (2) study of the mineralogical composition of the clay fraction of a great number of Spanish soils.

Investigations on the identification of natural silicates resulted in the discovery, by E. Gutiérrez Ríos and L. Hernando (1947, 1948), of bentonite deposits in Spanish Morocco. The genesis of the montmorillonite of this deposit was the object of research by E. Gutíerrez Ríos and F. González García (1949) who concluded that it was formed by the action of water on andesites and that the contribution of Mg^{2+} by water plays an important role in the genesis of montmorillonites. The transformation takes place in an alkaline medium and is initiated by hydration of the crystalline lattice of the rock feldspar.

Employing the calculation method suggested by Ross and Hendricks, Gutiérrez Ríos and González García (1948) determined the mineralogical formulas of the bentonite of Moroccan deposits. They concluded that the bentonite minerals are members of the montmorillonite-beidellite series, and that some of them represent very advanced substitution of Si^{4+} by Al^{3+}.

V. Aleixandre (1949) later established the halloysitic nature of the Maazza deposits and the montmorillonitic character of the green and white smectitic clays of Sierra de Gador (Almería).

In their study of the Sierra de Nijar (Almería) deposits, J. L. Martín Vivaldi and F. González García showed that the mineral is fundamentally a member of the montmorillonite-beidellite series, revealing a high degree of isomorphous substitution of Al^{3+} by Mg^{2+} and Fe in octahedral coordination (González García and Martín Vivaldi, 1949; Martín Vivaldi and González García, 1951). The electron microscope has revealed the existence of a high concentration of fibrous particles which must be related to montmorillonite, although the literature fails to mention this morphology in minerals of the montmorillonite-beidellite series.

A. Hoyos de Castro and M. Delgado (1949) have investigated the genesis of

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the kaolin deposits of Carataunas (Granada) and have concluded that the kaolin is the result of the alteration of an eruptive rock. First, sericite was formed by hydrothermal metamorphosis, through the agency of alkaline solutions. Later, transformation of sericite by means of hydrothermal processes or weathering led to the formation of kaolin.

Hoyos de Castro and Delgado (1952) have also investigated the genesis and character of the material known as "launa."

M. Delgado (1953) has studied two serpentine deposits, one in Sierra Nevada (Granada) and the other in Sierra Bermeja (Málaga). He concluded that the former is hydrothermal in origin and is possibly derived from a pyroxenite. The second deposit seems to be of hypogenic origin.

J. L. Martín Vivaldi and J. Cano Ruiz (1953) have investigated the sepiolites of the Vallecas (Madrid) and Cabañas de la Sagra (Toledo) deposits and have established their approximate empirical formula as $6SiO_2 \cdot 4RO \cdot 7H_2O$, where R is mainly Mg^{2+}, with some Fe and Al^{3+} in isomorphic substitution. Of the seven molecules of water, four are lost at temperatures below 300° C and must, therefore, represent completely reversible hygroscopic water.

A later detailed study of the dehydration process in sepiolite (Martín Vivaldi and Cano Ruiz, 1956) has enabled them to establish a closer agreement with the types of water postulated by Nagy and Bradley (1955). Of the seven water molecules, three are in the channels, are totally reversible, and are given off up to about 100° C; two are coordinated water molecules and are given off up to about 400° C. A portion of them is lost in the molecular water region and is reversible. A part of the lattice water molecules (0.5 mol) is lost between 400° and 500° C (water of the charge-compensating cations). Above 500° C the true lattice water (1.5 mol) is lost.

These authors (1956) in another study have suggested that minerals of the palygorskite-sepiolite group occupy the discontinuity interval existent between dioctahedral and trioctahedral minerals.

F. González, F. Tristán and M. Chaves (1954) have described the vermiculite from a Badajoz deposit.

V. Aleixandre and D. Alvarez-Estrada (1949) and J. García Vicente (1951) have investigated several talc samples from deposits in Almería, Boñar (León), and Gerona. The influence of chemical composition on the position of the endothermic peak characteristic of talc has been described: In the pure sample it is found at temperatures over 1000° C, while in the impure it sets in around 950° C. The authors suggest that this is due to the mineralizing action of impurities (dolomite, chlorite, quartz) which favor the transformation of talc into proto-enstatite.

M. Muñoz Taboadela and J. Ramirez (1953) have studied the relation of trace elements to the origin of certain clay minerals. Metahalloysite (Valdemorillo, Madrid) and pure gibbsite (Puente de Arce, Santander) contained a smaller proportion of alkaline and alkaline-earth cations and, particularly, no Li^+. The proportion of the Li^+ was low in such minerals as sepiolite (Cabañas de la Sagra, Toledo) and leathery sepiolite (Cerro de Almodóvar, Madrid), and high in saponite (Molinos, Teruel). The proportion of alkaline and alkaline-earth cations measures, to a certain degree, the eluvial or illuvial conditions of formation of the minerals.

In close parallellism to these investigations on pure silicates, the Instituto de

Edafología has undertaken work on the mineralogical composition of some rocks and clays extracted from soils or employed in the ceramic industry. Silurian shales have been studied by J. M. Albareda, V. Aleixandre and M. C. Sánchez Calvo (1949, 1951). In all these shales (besides quartz which occurs abundantly as very fine grains) the dominant minerals are micas, especially muscovite. Kaolinite is also present, though in smaller proportion. Chlorite and a mixed-layer mica-chlorite mineral (García Vicente and Sanchez Calvo, 1954) are present as accessory minerals.

Albareda, Aleixandre, and Sánchez Calvo (1952) have investigated clays extracted from soils formed from Silurian shales, and have observed that the predominating mineral is illite, sometimes associated with kaolinite. Thus, muscovite has been altered to illite by weathering.

The above mentioned workers have also determined (personal communication) those minerals present in the *braunlehm* clays of Spanish Continental Guinea. It was found that the greater part of these clays contains from 50 to 90 percent kaolinitic minerals. The remainder is made up of crystalline hydroxides such as gibbsite and lepidocrocite (Figs. 1, 2) and amorphous matter. Hematite is present but in very small amounts. The presence of metahalloysite has been confirmed through electron microscopy.

M. Alía, T. Alvira and M. Muñoz Taboadela (1952) have also studied the clays of Continental Guinea soils and have found in these equatorial soils (derived principally from migmatites) metahalloysite, gibbsite, and goethite. The goethite has contributed in a great measure to formation of loose concretions at some horizons. A. Hoyos de Castro and Rodriguez Martínez (in press) have recently studied the soils and clays of Insular Spanish Guinea and have found a similar group of clay minerals.

The study of the clay fraction of Spanish soils raised a problem as to the most appropriate particle size for the characterization of the specific clay minerals present. In order to study this problem, J. M. Albareda, V. Aleixandre and J. García Vicente (1950) took the clay fraction of 13 horizons of Spanish soils which had developed under different climatic conditions and subdivided it into three other fractions of the following diameters: less than 0.8μ, 0.8 to 1.13μ, and 1.13 to 1.97μ. It was found advisable to employ the fraction made up of particles having a sedimentation velocity of 10 cm/ 24 hr in the mature soils, and of particles having a sedimentation velocity of 10 cm/ 48 hr in the poorly developed soils.

Starting from typically Peninsular soils, M. Muñoz Taboadela (1952, 1953) has found the following correlations between soil types and clay mineral assemblages:

A. *Arid zone soils.* — Present conditions: mean annual rainfall, 300 to 700 mm, of irregular distribution throughout the year; mean annual temperature, 12 to 18° C.

1. Red calcareous soils. Extensively distributed in the arid zone of Spain, contain about one percent of organic matter; pH 7 to 8. Contain 10 to 40 percent of red clay with a cation-exchange capacity of about 30 to 40 meq/100 g and a base saturation of more than 90 percent. These soils include the Mediterranean *terra rossa*. The clay minerals are dominantly illite with some kaolinite. The color of these soils is due partly to colloidal iron in the form of hematite.
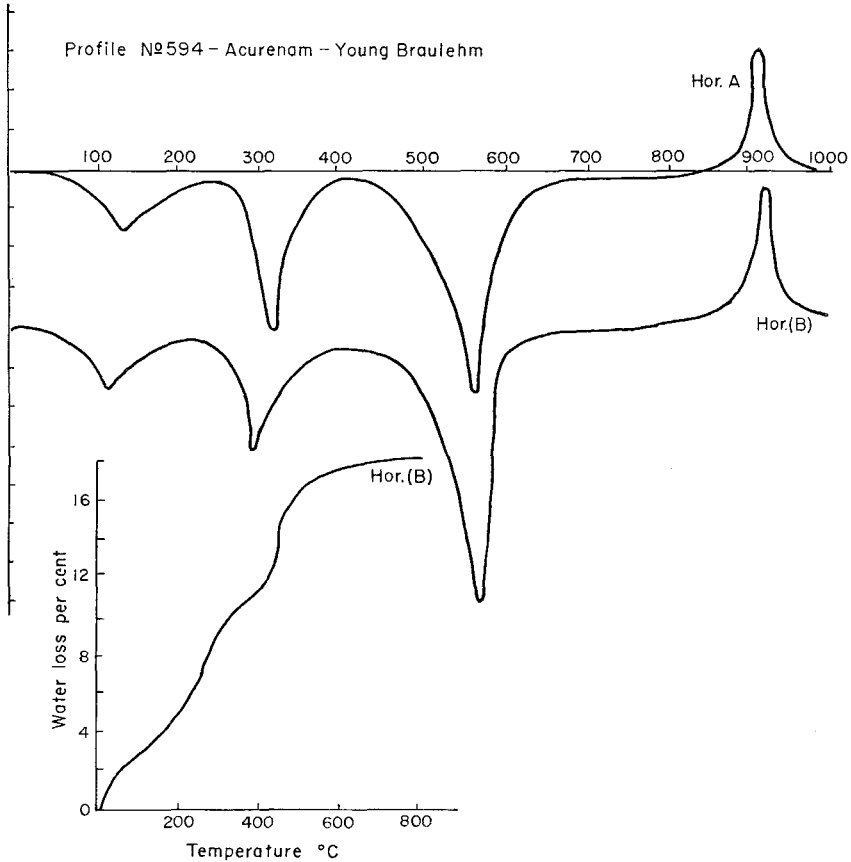
FIGURE 1. — Differential thermal curves and water-loss curve, Profile no. 594, Acurenam, Young Braunlehm.

    2. Andalusian black soils. Widespread in southern Spain. Gray to dark-gray soils, especially from the low-lying areas, containing one to three percent of Ca-saturated humus, and yielding 30 to 60 percent of base-saturated clay having a cation-exchange capacity over 50 meq/100 g. The clay minerals are dominantly montmorillonoid and accessory illite.

    B. *Humid zone soils.* — Present conditions: mean annual rainfall, 1000 to 1400 mm, and mean annual temperature 10 to 13° C. The iron-humus podsols from Asturias, N. Spain, which developed generally from pure sandstone containing only a trace of kaolinite, produced a clay mineral assemblage of dioctahedral illite (especially in the illuvial horizons) and kaolinite (specially in the eluvial horizons). Some Al^{3+} and Fe^{3+} in the colloidal fraction occurs as gibbsite and goethite in the illuvial levels.
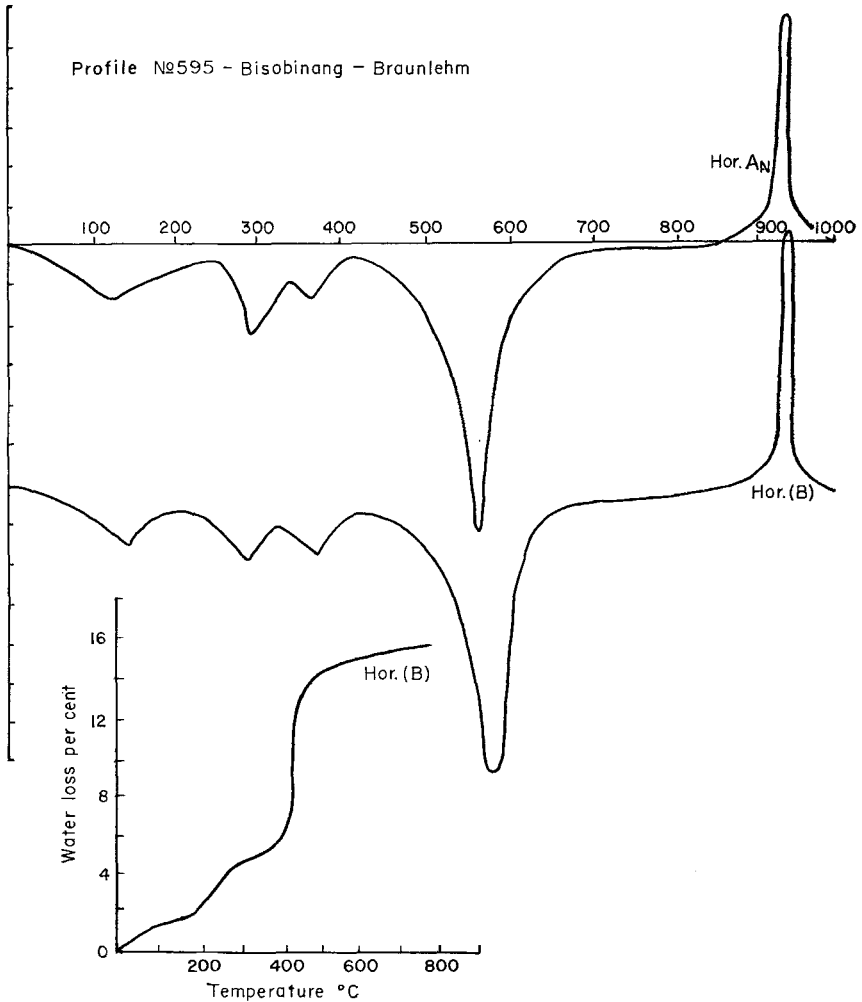
FIGURE 2. — Differential thermal curves and water-loss curve, Profile no. 595, Bisobinang, Braunlehm.

The irregular distribution of clay throughout the profile suggests the following evolution of clay minerals in the podsol profile: Formation of illite in the *B* horizons, and weathering of illite to kaolinite in the *A* horizons.

PHYSICO-CHEMICAL BEHAVIOR OF SILICATES

From a quantitative point of view, E. Gutiérrez Ríos and J. L. Martín Vivaldi (1949) have studied the capacity of kaolinite and montmorillonite to enter into

association with water. A series of alkaline and alkaline-earth bentonites and kaolinites were prepared and the hydrations at different vapor pressures (over 70, 50 and 30 percent sulfuric acid, at 20° C, corresponding to partial vapor pressures of water of 1.30, 6.50 and 13.15 mm Hg at 20° C) were studied. Through these experiments the authors have formulated the following empirical equations:

$$\text{Alkaline bentonites} \quad \ldots \quad \ldots \quad H = \frac{bp}{i} + \beta \, \frac{ze}{r^2}.$$

$$\text{Alkaline-earth bentonites} \quad \ldots \quad \ldots \quad H = \frac{bp}{i} + 108 \, i + \beta \, \frac{ze}{r^2}.$$

where H represents hydration, b is a constant, p the partial water-vapor pressure in mm of mercury, i the number of exchange cations per gram of substance, β a constant, e the charge of the electron, z the number of electrical charges of the exchange cation, and r the radius of the exchange cation. The quotient ze/r^2 is the polarization capacity of the exchange cation (Goldschmidt). Thus, at constant pressure there is an approximately linear relationship between the hydration of the substance and the polarization capacity.

These formulas have been corroborated both by our data and others, and the agreement between the experimental and calculated values is of the order of magnitude which corresponds to the methods employed.

The value b is a constant for each type of mineral; for Spanish Morocco and Mississippi bentonites consonant values of 4.5×10^{-6} and 4.3×10^{-6} have been obtained respectively; for kaolin the value is 8.1×10^{-9}. The constant b is independent of the nature of the exchange cations. Therefore, the amount of water represented by bp/i behaves as if its union were motivated only by the surface of the crystalline layer. The β factor depends on the nature of the

material, among other factors, and consequently the term $\quad \beta \, \frac{ze}{r^2} \quad$ depends on

the material and on the exchange cations.

The logarithmic representation of the imbibition phenomenon shows three straight spans which are attributed first to the predominance of capillary imbibition, secondly to the intermicellar type, and, finally to imbibition of an osmotic nature.

J. Cano Ruiz and J. L. López González (1955) have extended the use of this process to other layer-lattice silicates and have studied montmorillonite, vermiculite, illite and sepiolite. A marked difference between silicates revealing laminar expansion and those lacking it can be observed. The osmotic gradient of the nonswelling silicates is of the same order of magnitude as that of silica gel prepared and investigated by the authors.

A. Hoyos de Castro and J. Rodríguez (1952, 1954) have studied the imbibition of a bentonite the surface of which has been modified by thermal treatment. The modifications due to thermal treatment have also been studied by F. González García and S. González García (1953) in silicates of the montmorillonite-beidellite isomorphous series. Samples of montmorillonite saturated by cations having a strong electrostatic field and a high polarization capacity (Li⁺, Mg²⁺, Zn²⁺, Ce³⁺, H⁺) are dehydrated irreversibly when heated at temperatures below those required for elimination of hydroxyl water.

Samples saturated with cations having a weaker electrostatic field (Ba^{2+}, K^+, Rb^+) are dehydrated reversibly under the same conditions of treatment.

E. Gutiérrez Ríos and J. D. López González (1952; 1955) have also studied the action of strong acids on members of the montmorillonite-beidellite isomorphous series. Chemical study shows that the constituent cations of the crystalline lattice are dissolved in an amount which diminishes in the measure in which the polarization capacity of the cations increases; i.e., $MgO > Fe_2O_3 > Al_2O_3$.

	Mg^{2+}	Fe^{3+}	Al^{3+}
ze/r^2	3.29	6.68	9.23

E. Gutiérrez Ríos and J. Cano Ruiz (1954) have undertaken a thermodynamic study of ion exchange and have formulated an equation for cation exchange. On the basis of Vanselow's equation they have also considered the hydrated radii of the cations taking part in the exchange. The larger the radius of the cation in solution, the less intense will be its electrostatic field, and, therefore, the smaller will be the electrostatic attraction toward the negative charge harbored in the adsorbent; consequently, the power of the cation to replace others is smaller. Therefore, it is considered that the number of moles which are adsorbed at any instant is inversely proportional to the hydrated radius of the adsorbed cation, $1/r$. Appending this consideration to those on which Vanselow's equation is based, they develop equations for cation exchange between monovalent ions and between mono- and divalent ions.

The authors have carried out an exhaustive experimental substantiation of these equations employing both their own data and those of other authors, such as Vanselow (1932) and Magistad, Milton, and Marby (1944). The equilibrium constant of ion exchange is considered as a function of the hydrated ionic radii.

E. Gutiérrez Ríos and C. del Pino Vázquez (in press) have applied this equation of Gutiérrez Ríos and Cano Ruiz (1954) to the exchange equilibrium between hydrogen and alkaline ions, taking into account the difficulties evoked by consideration of the hydrogen ion in the different proposed equations. The experimental work was carried out with Volclay bentonite and "duolite" ion-exchange resin.

TECHNICAL APPLICATIONS

The study of certain Spanish silicate deposits revealed their excellent properties for industrial applications and has furthered technical work.

Research on Moroccan bentonite deposits and the substantiation of their quality induced E. Gutiérrez Ríos (1949) to study the technological character of these bentonites in order to establish their industrial utility as well as those applications more adequate to the nature of the material. Two different types of products cover the field of suggested application: colloidal bentonite and activated bentonite. Both were obtained and their quality compared favorably with that of similar foreign products. The use of the materials obtained in decoloration of oils, soap manufacture and preparation of compounds associated with sulfur (of excellent use as fungicides) was specifically studied.

Investigations of talc deposits led V. Aleixandre and D. Alvarez-Estrada (1952) to initiate their work on the preparation of steatite ceramic bodies using Spanish talc and to study its dielectric properties. Pastes of various compositions were prepared employing talcs from different sources, and the following tests were carried out: (1) Variation of dielectric losses and dielectric constant with frequency; (2) variation of dielectric losses and dielectric constant with temperature; (3) variation of superficial and volume resistivity with relative humidity and temperature; and (4) dielectric rigidity.

The results corroborated the excellent properties of Tíjola talc. Dielectric losses diminish with frequency till a minimum is attained. Increase in temperature strongly increases the dielectric losses but, on the other hand, exerts no influence on the dielectric constant. Volume resistivity diminishes rapidly with

increasing temperature in agreement with the exponential equation $\rho = Be^{a/T}$

where B and a are constants.

The mineralogical composition of the clays employed in ceramic industry and its influence on their technical properties was the object of work carried out by V. Aleixandre and A. García Verduch (1950, 1951). The following technical properties were studied: plasticity, viscosity, thixotropy, sedimentation volume, rate of water loss through the mass, contraction on desiccation, porosity during desiccation, volume variation on calcination, porosity and sinterization, and mechanical resistances in desiccated pastes.

The relations between plasticity and mineralogical constitution of the materials have been elucidated.

In the study of the viscous behavior of clay suspensions it has been observed that, both when diluting the suspension and when adding NaOH, a rectification of the flux-hydrostatic pressure curves takes place. At the same time mobility increases and the yield value decreases.

In the tests carried out on the thixotropic behavior of clay suspensions with the torsion consistometer, the expression in absolute units of the variation of rigidity with time has been attained. Thixotropic curves have been obtained for various different materials.

In diagrams of contraction and changes in porosity during desiccation the different forms in which water is retained in clay masses have been exhibited and it has been fully substantiated that the course of this phenomenon in different materials allows for a clear differentiation of their mineralogical character. Contraction by desiccation increases in the following order: Kaolins, illitic clays, and montmorillonitic clays. Porosity increases in the reverse order.

V. Aleixandre, J. Robredo and J. García Vicente have undertaken research on the clays in Spanish molding sands, classifying them in accordance with the mineralogical composition of the agglomerating fraction (Aleixandre, Robredo Olave, and González Peña, 1954; García Vicente and Robredo Olave, 1955). They also made the following technical determinations: (1) Granulometry of the sandy fraction; (2) compression resistance (in green molding sand); (3) apparent density; and (4) permeability (in green molding sand).

The results obtained are well interpreted by the hypothesis of Grim and Cuthbert, which admits the existence of blocks in the form of a wedge in molding earths, in order to explain the agglomerating action of the clay in those earths.

It has been observed that the factor which has the greatest influence in resistance to compression in green molding sands is the nature and proportion of the agglomerant.

Green permeability is influenced, above all, by the granulometry of the sand fraction: this dependence can be explained by Jasson's equation which establishes a relation between permeability and the fineness index A. F. A., and the density of the prepared sample after the attack.

It has been observed that if the molding earth has a low content of agglomerant, the permeability depends only on the granulometry of sand and is independent of the mineralogical nature of the agglomerant.

V. Aleixandre, J. García Vicente and C. Sánchez Conde (1955) have studied several Spanish quartzites and their transformation into tridymite by the action of different mineralizing agents (including ferric oxide and lime), at temperatures between 1200° and 1420° C.

Dilatometric curves are of use in following up tridymitic transformation. The quartz peak is situated around 575° C while that of tridymite occurs at about 150° C.

X-ray diffraction shows that transformation to tridymite is more intense when the mineralizing agent contains ferric oxide.

Finally, J. M. Albareda, V. Aleixandre, and T. Fernández (1953) have investigated the influence of the mineralogical composition of clays and of exchangeable cations in the catalytic oxidation of ethyl alcohol in the vapor phase, showing that, with montmorillonite, the maximum yield is found around 375° C, while with kaolin at 400° C (the highest temperature attained) it continued to increase. Montmorillonite produces more CO_2 than kaolin at every temperature tested.

Among all the exchange cations tested with montmorillonite, silver and copper give the highest aldehyde yields.

These materials are activated by means of heat and a stream of air. This process is more economical than that employed in activating silver and copper when they are used as metals or as their oxides.

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I deeply acknowledge the kind invitation extended to me by the Clay Minerals Committee which tendered me the opportunity to take part in this Conference, in the course of which I have described the different aims of the work undertaken on clay minerals by the Instituto de Edafología y Fisiología Vegetal.

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