Clays and Clay Minerals, Vol. 39, No. 2, 211–218, 1991.

HIGH-CHARGE SMECTITE IN SPANISH "RAÑA" SOILS

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Abstract—In a study of "raña" soils of central Spain, hydroxy-interlayered 2:1 clay minerals were identified in the upper horizons and high-charge smectite in the lower horizons, with kaolinite the most abundant phyllosilicate. The high-charge smectite showed a basal spacing of 18 Å on Mg-saturation and glycerol solvation and 10 Å on K-saturation and air-drying. It is concentrated in the coarse fractions and appears to be basically a beidellite in the fine-silt fractions and a montmorillonite in the clay fractions. Pre-existing illite was probably transformed into hydroxy-interlayered 2:1 clays in the surface horizons, whereas high-charge smectite formed in the deeper horizons. These minerals, which were apparently not stable in the existing soil conditions, were the first stage in the degradation process of illite. The stable mineral in these soil profiles was kaolinite.

Key Words—High-charge smectite, Hydroxy-interlayer clays, Illite, Layer charge, "Raña" soils, Soil clay.

INTRODUCTION

The weathering of K^+-bearing micas has been known for some time to result in the formation of expandable 2:1 clay minerals. Bray (1937) pointed out that the removal of K from mica produces a beidellite-type mineral having cation-exchange properties. The process is usually interpreted as a mica-to-vermiculite-to-smectite continuous sequence. According to Kittrick (1973), vermiculite may transform from mica initially, but it is a fast-forming, unstable intermediate. During this transformation, interlayer K^+ is replaced by hydrated cations, and the layer charge is reduced (Fanning *et al.*, 1989).

Some artificial weathering studies, however, have shown that micas have been directly transformed to smectite (Huff, 1972; Robert, 1973). Smectites weathered from micas are likely to be tetrahedrally substituted, approaching the beidellite end member in chemical composition (Özkan and Ross, 1979). They usually show a behavior midway between those of normal smectite and vermiculite, and have been called high-charge smectite, low-charge vermiculite, or transformation smectite. High-charge smectite has been defined as a smectite that shows a basal spacing of 18 Å on Mg-saturation and glycerol-solvation and 10 Å on K-saturation and air drying (Egashira *et al.*, 1982). High-charge swelling phyllosilicates have been reported in many soils as a weathering product of mica (Robert *et al.*, 1974; Stoch and Sikora, 1976; Nash, 1979; Egashira and Tsuda, 1983; Senkayi *et al.*, 1983, 1985; Badraoui *et al.*, 1987). The formation of high-charge smectite may require dioctahedral mica, whereas trioctahedral mica is likely to be transformed into vermiculite (Egashira and Tsuda, 1983). The importance of the high-charge 2:1 minerals for crop production has recently been outlined by Chen *et al.* (1989) due to their capability for fixing NH_4^+ and K^+.

The word "raña" is used for alluvial-fan type formations, Pliocene-Quaternary aged, originating from shale-quartzite regions, and associated with significant tectonic readjustments, which range from the phase of levelling and filling of Tertiary basins to the deepening of the oldest terrace. Such areas are flat or have only gently inclined surfaces; they contain highly developed soils having marked hydromorphic characteristics. In Spain, such "raña" material covers an area of about 400,000 ha and is found in large areas of the Iberian peninsula. Spanish "raña"-type soils were studied by Espejo (1985, 1987), Vicente *et al.* (1986), Rodríguez-Pascual *et al.* (1987), García-González and Aragoneses (1988, 1990), Sánchez-Camazano *et al.* (1988), and Aragoneses (1990).

The aim of the present paper is to report the occurrence of high-charge smectite in Spanish "raña" soils and to relate the properties of the smectite to its genesis in an attempt to increase our understanding of the processes of formation and development of these formations.

MATERIALS AND METHODS

The zone studied is in the Province of Guadalajara in the northeast center of the Iberian peninsula. The study centred around the Membrillera, Robledo de Corpes, Bustares, and Mesa del Pino areas, subsequently abbreviated as ME, RC, BU, and MP, respectively (Figure 1). The soil profiles in the last three areas were developed from "raña" formations, whereas those in ME area originated from materials that clearly do not belong to the oldest terrace or to raña, but which represents a transition area between the so-called "upper-raña" (zones above 1100 m, RC, BU, and MP) and "lower-raña" (zones below 930 m, southern ME). All the profiles studied were deep, acidic, had marked hydromorphic characteristics and low organic matter

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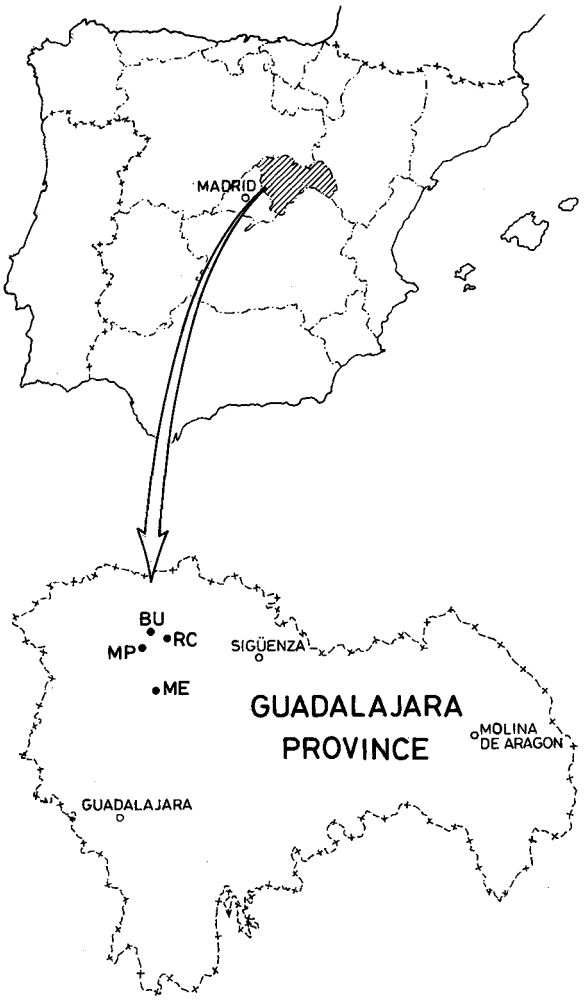


Figure 1. Map showing location of study area.

content, were usually very stony, especially on the surface, and showed a high degree of weathering (see also Table 1).

Samples were taken from each horizon of the four studied profiles. The clay fraction (≤ 2 μm) and the fine-silt fraction (2–8 μm) were extracted by means of sedimentation. The size fractions were treated with hydrogen peroxide to eliminate the organic matter. Three different treatments were carried out for Mg-saturation of the clay and fine-silt fractions: (1) triple washing with 0.5 M Mg chloride; in the first treatment, the sample was kept in contact with the solution for 24 hr (sMg procedure); (2) double washing with 1 M Na acetate and then four times with 0.5 M Mg chloride (Na-sMg procedure); the first treatment with each salt lasted for 24 hr; and (3) the same as (2), but keeping the temperature at 70°C in a water bath (70Na-sMg procedure). All samples of the clay fraction and of the fine-silt fraction containing substantial smectite were Mg-saturated using the normal procedure (sMg). The other treatments were used only for those samples for which the sMg procedure was not effective.

K-saturated samples of the smectite-rich horizons were prepared by treating them twice with 1 M Na acetate and then four times with 1 M K chloride at 70°C (70Na-sK procedure). Selected samples from the surface horizons were K-saturated using the normal procedure (sK) to obtain more information about possible interlayered hydroxide sheets.

Mineralogical identification was made by X-ray powder diffraction (XRD), using a Philips PW1130 diffractometer equiped with a graphite monochromator (CuKα radiation). XRD patterns were obtained from Mg-saturated clay and fine-silt fractions of each sample using: (1) random powder, and the following oriented aggregates; (2) air dried; (3) ethylene-glycol solvated; (4) glycerol solvated; (5) heated to 300°C for 3 hr; and (6) heated to 500°C for 3 hr. For the K-saturated samples, oriented aggregates were recorded (1) air dried at RH 55%; (2) ethylene-glycol solvated; and (3) glycerol solvated. Oriented specimens of the non-homoionic clay and fine-silt fractions (natural untreated samples) were also studied.

Samples having a higher smectite content were also analyzed for the Hofmann and Klemen (1950) effect. They were washed three times with 1 M Li chloride and then dialyzed to remove excess salt (sLi procedure). XRD patterns of air-dried and glycerol-solvated specimens were recorded. The samples were placed in a porcelain crucible and heated to 270°C overnight (270sLi procedure), and XRD patterns were recorded again (Greene-Kelly test, 1953).

The fine-silt fraction of one horizon per profile was

Table 1. Main characteristics of the soil profiles.

Profile[1]	Altitude (m)	Depth (cm)	Profile horizons	Classification (USDA, 1975)	pH H_2O 1:2.5	Drainage
ME	975	150	Au1, Au2, Bts, E, Btg, 2Btr	Ultic Palexeralf	Strongly acid	Poorly drained
RC	1140	110	Ap, Bt, Btg, BCtr	Aquultic Hapludalf	Very strongly acid	Poorly drained
BU	1180	75	A, AB, Bt, CBr	Aquultic Hapludalf	Very strongly acid	Imperfectly drained
MP	1130	110	Ap, ABg, Btg1, Btg2, BCr	Aquultic Hapludalf	Strongly acid	Imperfectly to poorly drained

[1] ME = Membrillera, RC = Robledo de Corpes, BU = Bustares, MP = Mesa del Pino.

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treated with (1) sodium carbonate (Follett *et al.*, 1965) and (2) dithionite-citrate-bicarbonate (Mehra and Jackson, 1960), to eliminate all possible cementing agents. After each treatment the clay fraction was separated. XRD patterns of the oriented clay- and fine-silt subfractions were recorded: (1) air dried, (2) ethylene-glycol solvated, (3) heated to 300°C for 3 hr, and (4) heated to 500°C for 3 hr. Some samples were previously Mg-saturated using the 70Na-sMg procedure described above.

Semiquantitative estimations of quartz, feldspars, goethite, and total phyllosilicates were obtained from XRD random powder patterns, integrating the area of the diffraction maxima at 4.26, 3.25, 4.16, and 4.44 Å, respectively, and using the intensity factors given by Schultz (1964) and Biscaye (1965). Approximate abundances of kaolinite, illite, paragonite, smectite, and hydroxy-interlayered clay were estimated in a similar way, using the oriented aggregate patterns; peak areas at 7.2 (kaolinite), 10.0 (illite), 4.8 (paragonite), 16.9 and 14.1 Å for ethylene glycolated samples (smectite and hydroxy-interlayered clay) were measured. Thus, given the method used, the values shown in Table 2 are not truly quantitative, but were used only as an internal measure.

RESULTS

Clay mineral identification

The XRD patterns of the Mg-saturated samples (sMg procedure) indicate that kaolinite, illite, and 14-Å minerals are the major components of the clay and fine-silt fractions of the profiles. In the surface horizons the 14-Å peak did not shift to lower angles when the sample was solvated with ethylene glycol or glycerol (Figure 2). After heating at 300°C, that peak became a broad band, slightly shifted to lower spacings, and disappeared after heating at 500°C. This clearly indicates the absence of chlorite. The K-saturated sample (sK procedure) clearly showed the 14-Å peak (Figure 2). According to Robert (1975), all these features indicate the existence of hydroxy-interlayered 2:1 clay minerals.

In the B horizons the 10-Å peak of some samples was markedly asymmetric towards lower angles and became more asymmetric when the sample was solvated with organic compounds. For other samples, peaks at about 11–12 Å were noted (Figure 3), possibly due to either the presence of an interstratified mineral or to the fact that Mg^{2+} was not capable of substituting for the interlayered cation in the smectite minerals. To clarify this situation, the samples that showed broad or diffuse reflections after Mg-saturation in the air-dried pattern were treated by the Na-sMg procedure. After such a treatment (Figure 3), the 001 reflection was found at lower angles, but in some samples not as far as 14 Å. The treatment was, therefore, repeated at 70°C (70Na-sMg procedure). This produced a peak

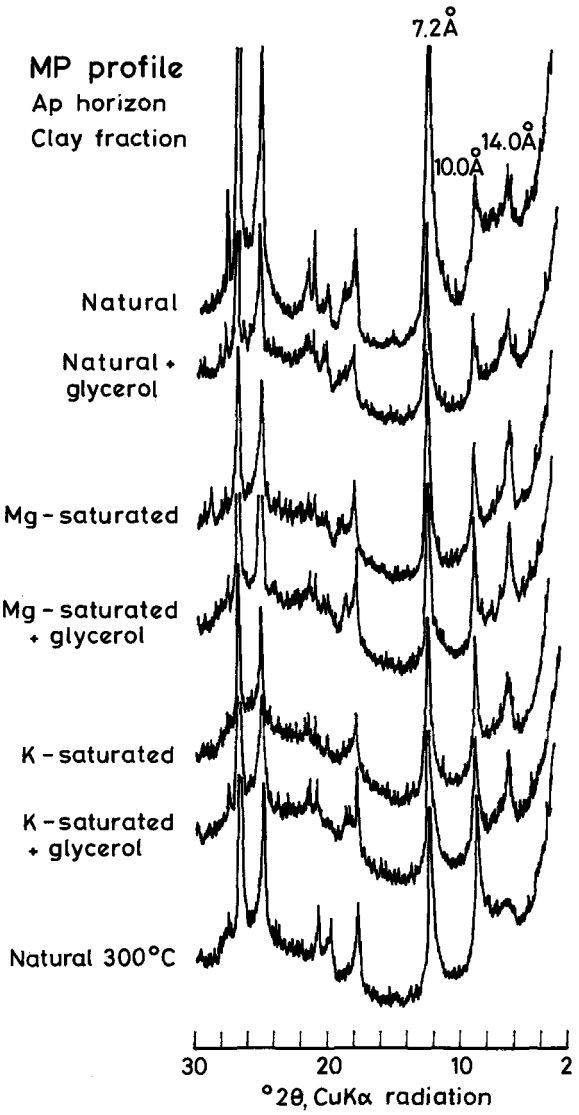


Figure 2. X-ray powder diffraction patterns of oriented aggregates after several treatments.

shifting to 14 Å for the air-dried, 17 Å for the ethylene-glycol-solvated, and 18 Å for the glycerol-solvated specimens (Figure 3). Thus, the sample probably contained a smectite in which the substitution of all interlayered cations by Mg^{2+} was achieved only by using the 70Na-sMg procedure.

The peaks at about 25 Å in patterns of the fine-silt fraction of the BCr (MP profile) and 2Btr (ME profile) horizons, after the 70Na-sMg procedure, indicate the presence of a small amount of regular interstratified mineral. The displacement of this peak to 28 Å after glycerol solvation (Figure 3) suggests that this mineral is a regular interstratified illite/smectite (I/S). Although in the literature I/S is often reported as a mineral of

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Table 2. Semiquantitative mineralogical composition (relative wt. % between samples) in the soil profiles of Membrillera, Robledo de Corpes, Bustares, and Mesa del Pino, Spain.

		ME										MP									
Fr	Hz	Ph	Q	F	G	K	I	P	S	Hy	In	Hz	Ph	Q	F	G	K	I	S	Hy	In
8–2 μm	Au1	38	55	7	—	6	29	—	—	2	—	Ap	48	44	4	4	8	36	—	4	—
	Au2	36	56	8	—	6	27	—	—	3	—	ABg	42	45	6	7	7	31	—	4	—
	Bts	63	31	3	4	20	40	2	tr	—	—	Btg1	72	15	tr	13	51	21	—	—	—
	E	38	55	3	4	10	23	1	—	tr	—	Btg2	73	12	tr	15	40	11	22	—	—
	Btg	70	20	2	8	43	20	tr	6	—	—	BCr	70	11	2	17	23	7	32	—	8
	2Btr	74	17	3	6	27	29	7	9	—	tr										
<2 μm	Au1	77	17	3	2	30	42	—	—	5	—	Ap	84	9	tr	7	40	34	—	9	—
	Au2	78	17	2	3	30	42	—	—	6	—	ABg	83	8	tr	9	41	36	—	6	—
	Bts	81	12	tr	5	37	37	4	2	—	—	Btg1	83	7	nd	10	60	20	—	3	—
	E	76	16	2	6	25	45	2	—	1	—	Btg2	90	nd	nd	10	68	11	12	—	—
	Btg	89	—	1	10	74	14	tr	1	—	—	BCr	93	nd	nd	7	75	8	9	—	—
	2Btr	93	—	tr	6	72	13	tr	7	—	—										
		RC										BU									
8-2 μm	Ap	33	59	6	1	6	25	—	—	2	—	A	38	52	5	4	7	30	—	tr	—
	Bt	70	16	1	12	37	28	3	2	—	—	AB	46	45	4	5	16	21	9	1	—
	Btg	65	18	2	15	34	26	3	3	—	—	Bt	75	12	2	12	38	13	24	—	—
	BCtr	63	21	5	11	27	15	4	17	—	—	CBr	70	14	3	13	45	6	19	—	—
<2 μm	Ap	82	10	2	7	42	29	3	—	8	—	A	80	13	1	6	33	42	—	4	—
	Bt	90	—	tr	9	60	21	3	7	—	—	AB	81	11	1	7	63	12	4	2	—
	Btg	88	—	tr	11	68	14	2	4	—	—	Bt	91	—	tr	9	70	16	4	—	—
	BCtr	91	—	tr	8	59	21	2	9	—	—	CBr	91	—	tr	8	78	9	4	—	—

Fr = fraction, Hz = horizon, Ph = phyllosilicates, Q = quartz, F = feldspars, G = goethite, K = kaolinite, I = illite, P = paragonite, S = smectite, In = interstratified illite/smectite, Hy = hydroxy-interlayered 2:1 clay minerals, — = not detected, tr = trace.

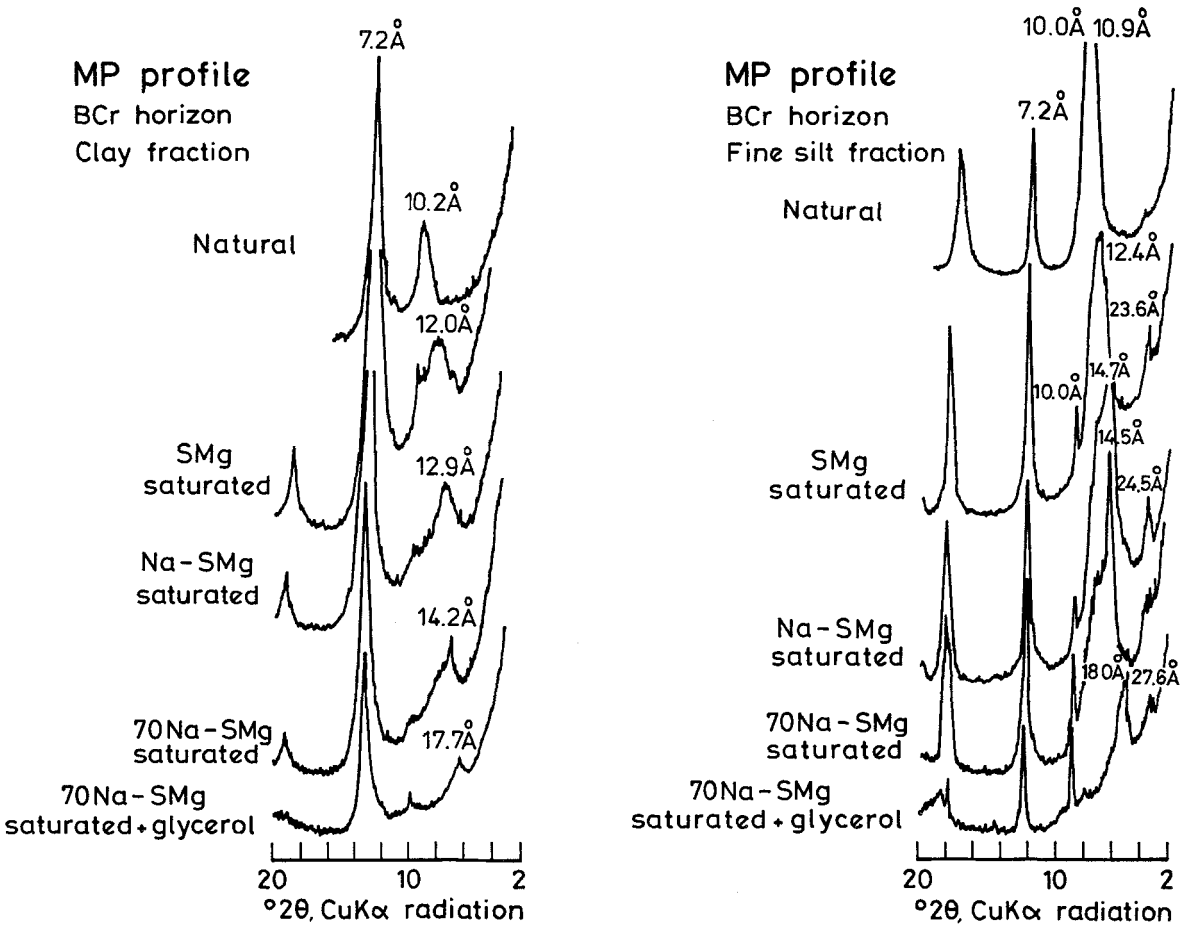


Figure 3. X-ray powder diffraction patterns of oriented aggregates after several saturation treatments.

extremely small grain size (Środoń, 1980), here, it has been found in the fine-silt fraction only.

To obtain a better knowledge of the smectite in these soils, the samples were also studied in their natural state. The XRD patterns of most samples showed (Figure 3) either an asymmetric peak at 10 Å, with asymmetry extending to 11 Å, or a peak at about 11 Å. These data suggest the existence of a K-smectite. Thus, the K content in these natural samples may have been responsible for the fact that the layers were collapsed, thereby making exchange with other cations difficult.

To determine the location of cationic substitution, samples of clay fractions were saturated with Li^+ and heated overnight at 270°C. These samples showed no expansion after solvation with glycerol (Figure 4), indicating that the charge in the smectite of the clay fraction was principally in the octahedral sheet. In contrast, the XRD patterns of the smectite in the fine-silt fractions showed a reflection or shoulder at 17.7 Å after solvation with glycerol. Thus, beidellite was probably the dominant smectite in the fine-silt fraction, and montmorillonite, in the clay fraction. Important differences were noted, however, in the 10-Å/17-Å intensity ratio of the sLi- and 270sLi-glycerol-solvated fine-silt samples, suggesting that not all the layer charge was due to tetrahedral substitution. Octahedral cationic substitution must also have been present. The layer charge of natural 2:1 clay minerals is commonly distributed over both sheets (Tsipursky and Drits, 1984).

The degree of collapse of the basal spacing by K-saturation and air-drying at 54% RH as a criterion for differentiating smectite from vermiculite (Harward *et al.*, 1969) was used in the present study. The collapse of the smectite to 10 Å took place in the samples of both the clay and fine-silt fractions (Figure 5). Thus, the layer charge of this mineral was closer to that of vermiculite and greater than would be expected for a typical smectite. The K-saturated mineral did not expand on ethylene-glycol solvation, indicating that K^+ tightly fixed the layers. The mineral, therefore, behaved like a smectite (peaks at 14.0 and 17.7 Å for the Mg-saturated air-dried and glycerol-solvated specimens, respectively) having high charge, as demonstrated by the collapsing to 10 Å in the K-saturated air dried at

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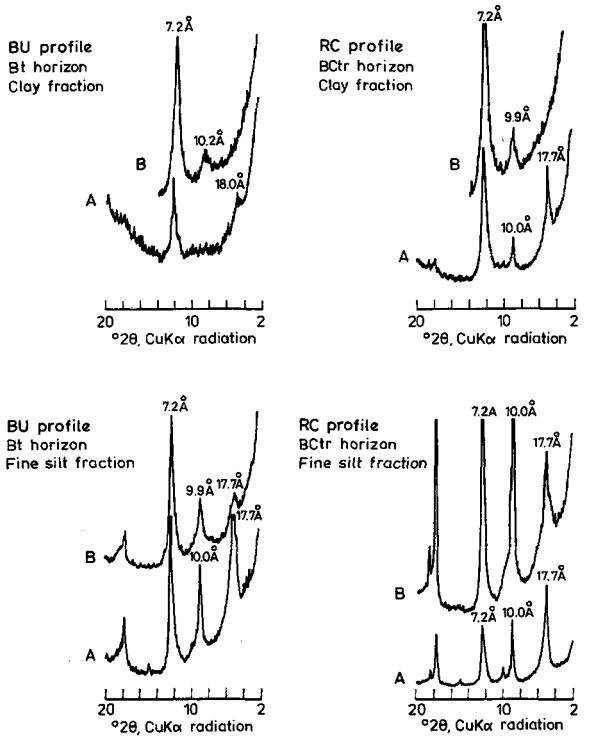


Figure 4. Greene-Kelly test applied to several samples: A, after sLi procedure and glycerol solvation; B, after 270sLi procedure and glycerol solvation.

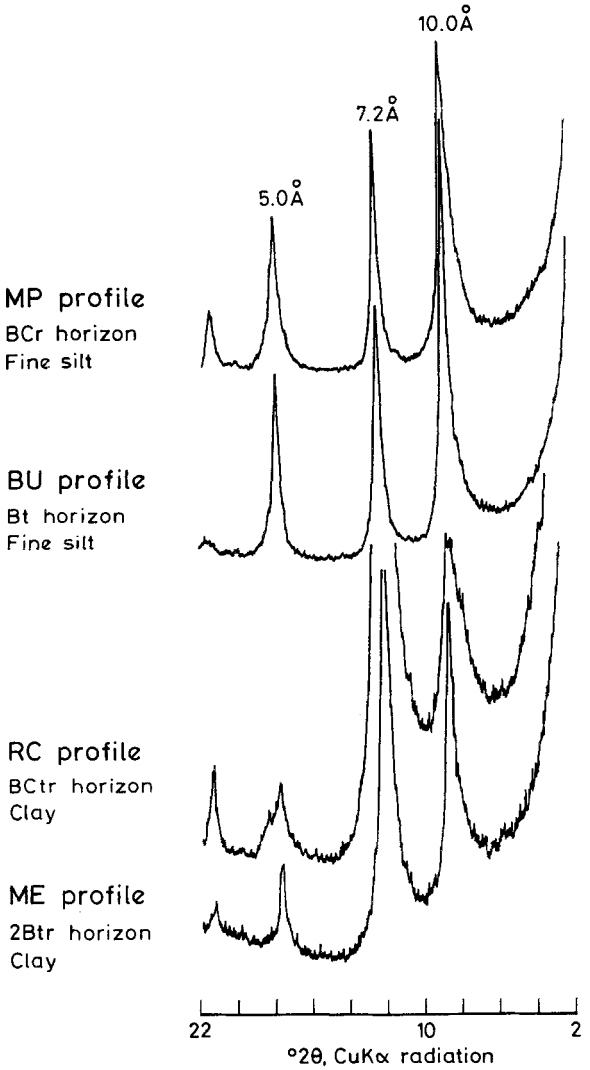


Figure 5. X-ray powder diffraction patterns of oriented aggregates of K-saturated samples (70Na-sK procedure).

54% RH sample. Therefore, this mineral can be termed as a high-charge smectite (Egashira *et al.*, 1982) having montmorillonite and beidellite characters in the clay and fine-silt fractions, respectively. This mineral was more abundant in the fine-silt than in the clay fraction, its proportion being greater in the non-surface horizons of the MP and BU profiles.

Semi-quantitative mineral composition

Table 2 shows the mineralogical composition of the four profiles. The phyllosilicate content in the clay fraction is high (76–93%), with a relatively high proportion in the fine-silt fraction (33–75%). The quartz concentration decreases markedly with depth, inversely with the phyllosilicate content. In the deeper horizons the illite content is markedly less, whereas the kaolinite content is greater. An exception is the eluvial E horizon from the ME profile, which is well defined and separate from the other horizons because of its greater content of primary minerals, compared with those in the underlying B horizons (García-González and Aragoneses, 1988).

Goethite was the only crystalline iron oxide identified in these soils, being concentrated in the fine fractions of the deep horizons. Small, rather uniform amounts of paragonite were also identified in the clay fractions of the ME- and RC-profiles, as well as in the fine-silt fraction (García-González and Aragoneses, 1990).

The high phyllosilicate and smectite concentrations in the fine-silt fraction might possibly have been due to the existence of aggregating agents. Iron oxide particles, for example, can react with clay particles via coulombic or non-coulombic forces (Schwertmann, 1988). On the other hand, siliceous and aluminous cements commonly bind clay particles into aggregates (Smith and Mitchell, 1989). To ascertain the possible existence of aggregating agents, two treatments were applied separately, one with the DCB reactive agent and one with sodium carbonate (to eliminate possible iron oxide and/or aluminosiliceous binding agents, respectively). Four fine-silt samples, one horizon per profile (Btg2 of MP profile, Bt of BU profile, BCtr of RC profile, and Btg of ME profile), were used. The DCB

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Table 3. Semiquantitative mineralogical composition (relative wt. % between samples) of fractions extracted from a fine-silt fraction after Na-carbonate treatment.

Profile[1]	Horizon	K	I	P	S	In
			Remanent fine silt			
BU	Bt	19	19	—	28	—
ME	2Btr	26	33	tr	9	tr
MP	BCr	25	10	—	22	4
RC	BCtr	27	47	4	17	—
			Remanent clay			
BU	Bt	29	23	—	13	—
ME	2Btr	20	43	tr	5	—
MP	BCr	23	7	—	32	3
RC	BCtr	18	23	2	22	—

K = kaolinite, I = illite, P = paragonite, S = smectite, In = interstratified illite/smectite, — = not detected, tr = trace.
[1] See Table 1 for abbreviations.

treatment did not produce a noticeable amount of clay fraction. Thus, iron oxides were probably not acting as cementing agents in these samples. The sodium carbonate treatment, on the other hand, produced a considerable amount of clay. The amount of high-charge smectite in the clay and remaining fine-silt fractions (both coming from the fine silt, Table 3) indicates that the accumulation of this mineral in the coarse fractions was not only due to the aggregating effect.

DISCUSSION

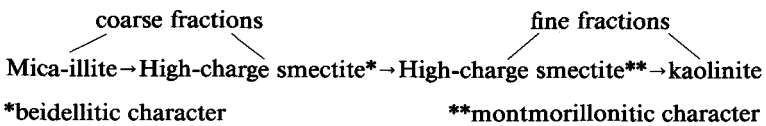
The high-charge smectite showed the following characteristics: (1) higher proportion in the fine silt than in the clay fraction; (2) high charge; (3) difficult opening of the layers, possibly due to the existence of interlaminar potassium. All this suggests that this mineral was formed by the transformation of the dioctahedral mica, illite (Robert *et al.*, 1974; Senkayi *et al.*, 1983, 1985; Rühlicke and Niederbudde, 1985). Thus, high-charge smectite was apparently an unstable mineral and appeared in the initial transformation stages of the illite. During weathering, the octahedral charge increased, changing the smectite character from beidellite (fine-silt fraction) towards montmorillonite (clay fraction).

The hydroxy-interlayered 2:1 clay minerals may have been formed from the illite transformation (April *et al.*, 1986; Farmer *et al.*, 1988) and its presence (Table 2) may be restricted to the surface horizons (Barnhisel and Bertsch, 1989). Illite was probably transformed into hydroxy-interlayered 2:1 clays in the surface horizons, whereas high-charge smectite was formed in the deeper horizons.

The I/S mineral found in two of the profiles probably represents a separate illite transformation. Środoń and Eberl (1984) suggested that I/S can form by the degradation of detrital illitic material. Removal of K^+ from illite-containing soils leads to the degradation of illite and the formation of smectite and interstratified material (Tributh *et al.*, 1987).

The stable mineral in these soil conditions was kaolinite. Its small grain size suggests that it was formed through a neoformation process (Koppi *et al.*, 1987), although a transformation from micas or expandable 2:1 minerals cannot be discarded. To understand the accumulation of kaolinite in the B horizons, the illuviation process should also be taken into account.

The mineralogical evolution of these soils could have been as follows:



ACKNOWLEDGMENTS

We thank Mrs. M. P. Lázaro, Ms. I. Antón, and Mr. A. Gómez for technical assistance. We are grateful for the valuable suggestions given by F. A. Mumpton, editor, and the referees. F. J. Aragoneses thanks the provision of a fellowship from the "Ministerio de Educación y Ciencia," Spain. This research was supported by CAICYT (Spain) under Project No. PR84/0140/C06.

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(Received 14 May 1990; accepted 19 November 1990; Ms. 2008)

https://doi.org/10.1346/CCMN.1991.0390213 Published online by Cambridge University Press