Electron microscopic study of the illite–smectite transformation in the bentonites from Cerro del Aguila (Toledo, Spain)

C. DE SANTIAGO BUEY*[†], M. SUAREZ BARRIOS[‡], E. GARCIA ROMERO*, M. C. DOMINGUEZ DIAZ[††] AND M. DOVAL MONTOYA*

* Dpto. de Cristalografía y Mineralogía, Fac. Geológicas, UCM, Madrid, [†] Centro de Microscopía Electrónica Luis Bru, UCM, Madrid, [‡] Dpto. de Geología, Area de Cristalografía y Mineralogía, Fac. Ciencias, Univ. de Salamanca, and [††] Dpto. de Química Agricola, Geología y Geoquímica, E.U. Santa Maria, UAM, Madrid, Spain

ABSTRACT: A mineralogical and microstructural study of bentonites from 'Cerro del Aguila' located in the Tagus Basin (Toledo, Spain) was carried out using XRD, SEM and TEM observations and chemical data obtained by TEM-EDX. The bentonites are mainly composed of trioctahedral smectite with a unit-cell formula $(Si_{3.76}Al_{0.24})(Al_{0.44}Fe^{3+}_{0.26}Mg_{1.81})Ca_{0.05}K_{0.19}O_{10}(OH)_2$ and small amounts of illite. The relationships between illite and smectite particles observed by SEM and TEM allowed the study of the weathering process of illite to form smectite through possible intermediate stages. The transformation begins as an exfoliation normal to the stacking direction and develops by opening of the interlayer spacing, the replacement of K^+ by hydrated interlayer cations and slight reorganization of the 2:1 layer structure. The so-called solid-state transformation process then proceeds by further dissolution and the formation of a colloidal phase acting as raw material in the growth of new phyllosilicates such as smectite.

Some bentonite exploitations are located in the Green Clays Unit of the Tagus Basin, Central Spain. These bentonites show a very special behaviour which makes them industrially useful. Many authors have investigated these materials from different points of view (Brell *et al.*, 1985; Galán *et al.*, 1986; García Romero, 1988; Cuevas, 1991; Leguey *et al.*, 1996). These studies show that bentonites are composed of a trioctahedral smectite with small amounts of illite, traces of kaolinite and occasionally sepiolite.

Although such bentonites essentially originate by neoformation, small amounts of detrital dioctahedral illite become unstable in a Mg-rich enviroment. Then, these illite particles undergo a weathering process forming smectite. Doval *et al.* (1985) indicated that part of the smectite found in this basin has been generated in a Mg- and Si-rich basin by transfomation of illite in a sedimentary environment. Illite–smectite transformation is a well-documented process in clay mineralogy. These transformation processes have been described by numerous authors: White (1950); Harder (1972); Robert (1972, 1973); Robert & Barshad (1973); Romero *et al.* (1992).

Recently, electron microscopy has been demonstrated to be a powerful tool in the study of these processes, because it allows the study of microtextural and genetic relationships between different minerals. In these types of studies it is usual to find mixed-layer minerals as precursors or intermediate stages of the transformation process (Ahn & Peacor, 1986a,b; Środoń *et al.*, 1990; Jiang *et al.*, 1990; Suarez *et al.*, 1994).

The objective of this work is to study the nature and characteristics of the textural relationships between the illite and smectite particles in the bentonites from Cerro del Aguila.

MATERIAL AND METHODS

Geological setting

The Tagus basin is an intramontane basin located in the Central Iberian Peninsula (Fig. 1). It is partially filled by Tertiary sediments deposited within a complex system of alluvial fans. These sediments originated as weathering products of peripheral mountain systems of igneous, meta-morphic and calcareous rocks distributed concentrically. Detrital facies from the margins of the basin are replaced towards the basin centre by mud flat facies, in which evaporite layers are gradually intercalated until they constitute a mainly saline core. The nature, distribution and characteristics of the different facies have been described by other authors: Calvo *et al.* (1989); Bellanca *et al.* (1992); Domínguez (1994).

The clays studied here form part of the mud flat facies and belong to the Green Clays Unit defined by Brell *et al.* (1985). This unit is more developed in the northern part of the basin than in its southern sector, where they only appear as two inselbergs: El Cerro del Aguila and El Cerro del Monte. Fifty samples were taken at separated points in four bentonite quarries located around the base of the Cerro del Aguila (arrow on Fig. 1) where the unit is ~120 m thick and is made of green or greenish-grey clays frequently bioturbated with a thin parallel lamination and intercalations of micaceous sands and rose clay levels, overlain by carbonate levels (García Romero *et al.*, 1988, 1990).

Methods

The mineralogical identification was carried out by X-ray diffraction (XRD) using a Philips 1130/90 diffractometer with Cu-*K*α radiation and a graphite monochromator. Random powder and oriented aggregates from the <2 µm and <0.5 µm fractions, previously homoionized with Na and Mg, were analysed.

The particle morphologies and textural relationships were examined using scanning electron microscopy (SEM), using a JEOL JSM6400, operated at 40 kV and equipped with a Link eXL X-ray energy dispersive detector.

Transmission electron microscopy (TEM) studies were carried out with specimens that retain their original textures. Oriented sections were made, according to the method proposed by Tessier
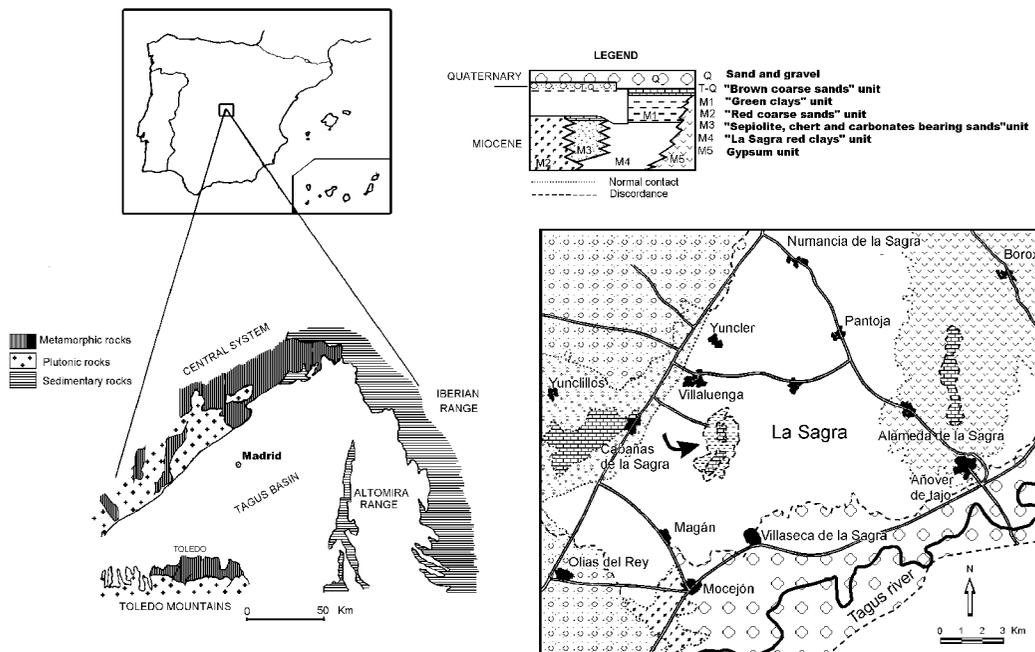

FIG. 1. Map showing the location and geological setting of the studied bentonite (García Romero, 1988).

(1984) where a small portion of sample is placed in Agar-Agar to protect it from later strains. The sample must then be hydrated and later the water from the structure is replaced by alcohol, and finally by epoxy resin. The resulting cured epoxy-clay complexes are sectioned by ultramicrotomy, to a thickness of 50 nm so as to be transparent to the electron beam. In this way, collapse due to quick dehydration during TEM observation is avoided and the natural texture of the sample is preserved. This method also shows evidence of swelling phases by penetrating hydrated interlayers such as those present in smectites (Tessier & Pedro, 1987; Vicente *et al.,* 1997). The TEM observations were performed in a JEM 2000FX operated at 200 kV and equipped with a Link AN10000 X-ray energy dispersive detector.

RESULTS AND DISCUSSION

Mineralogy

The samples are mainly composed of phyllosilicates with minor feldspar and quartz. Most of these phyllosilicates (75–90%) are trioctahedral smectites and XRD detected <10% illite.

AEM analysis

The AEM analysis performed on isolated particles shows a continuous range of compositions from dioctahedral aluminous mica to trioctahedral magnesian smectite, mainly saponite. The mean calculated structural formula for each group of mineral is:

Illite: $(Si_{3.09}Al_{0.90})(Al_{1.79}Mg_{0.23}Fe^{3+}_{0.08})$
$$K_{0.79}O_{10}(OH)_2$$
Saponite: $(Si_{3.76}Al_{0.24})(Al_{0.44}Fe^{3+}_{0.26}Mg_{1.81})$
$$Ca_{0.05}K_{0.19}O_{10}(OH)_2$$
Mixed-layer: $(Si_{3.35}Al_{0.65})(Al_{0.55}Fe^{3+}_{0.23}Mg_{1.95})$
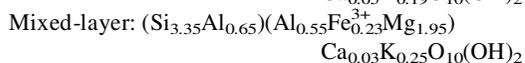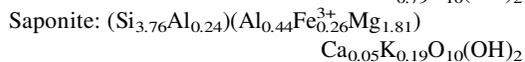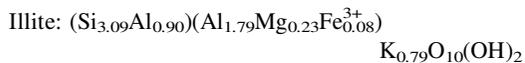$$Ca_{0.03}K_{0.25}O_{10}(OH)_2$$

Figure 2a shows that the larger the number of octahedral cations (changing from dioctahedral to trioctahedral), the lower the interlayer charge. Furthermore, there is a great chemical variation in Fe, Al and Mg contents. This particle composition is continuous, as seen in Fig. 2b (Velde, 1985) where an increase of Mg content (towards $3R^2$ pole) from illite composition can be observed. All the points analysed (except two which are closer to the stevensite composition) plot along a 'trend' from
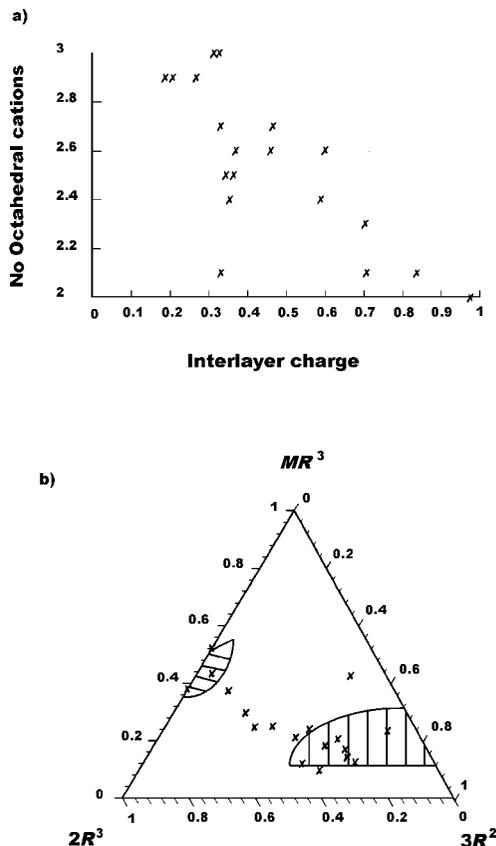

FIG. 2. (a) Relationship between the number of octahedral cations and interlayer charge. (b) Representation of AEM analysis after Velde (1985). $MR^3 =$ Na + K + 2Ca, $2R^3 = (Al+Fe^{3+})/2$, $3R = (Mg+Fe^{2+})/3$. ▦ Saponite composition ▨ Illite composition.

illitic towards saponitic composition. In any case, it is difficult to define a domain corresponding strictly to smectite composition. There are also intermediate compositional values which correspond to the different steps of the opening and degradation of layers linked to leaching of K and Al. These intermediate compositions could be related to mixed-layer minerals.

SEM

In general it can be observed that the total fabric is completely isotropic, formed by a random (non-oriented) array of particles. This flocculated fabric is typical of highly swelling soils with high salt

concentrations which reduces the interparticle repulsion (Bennett & Hulbert, 1986). Most of the sample has open structures (e.g. cornflake micro-structure, Fig. 3A) formed by smectite laminar particles which keep edge-to-edge and edge-to-face contacts. Smectite particles appear as small
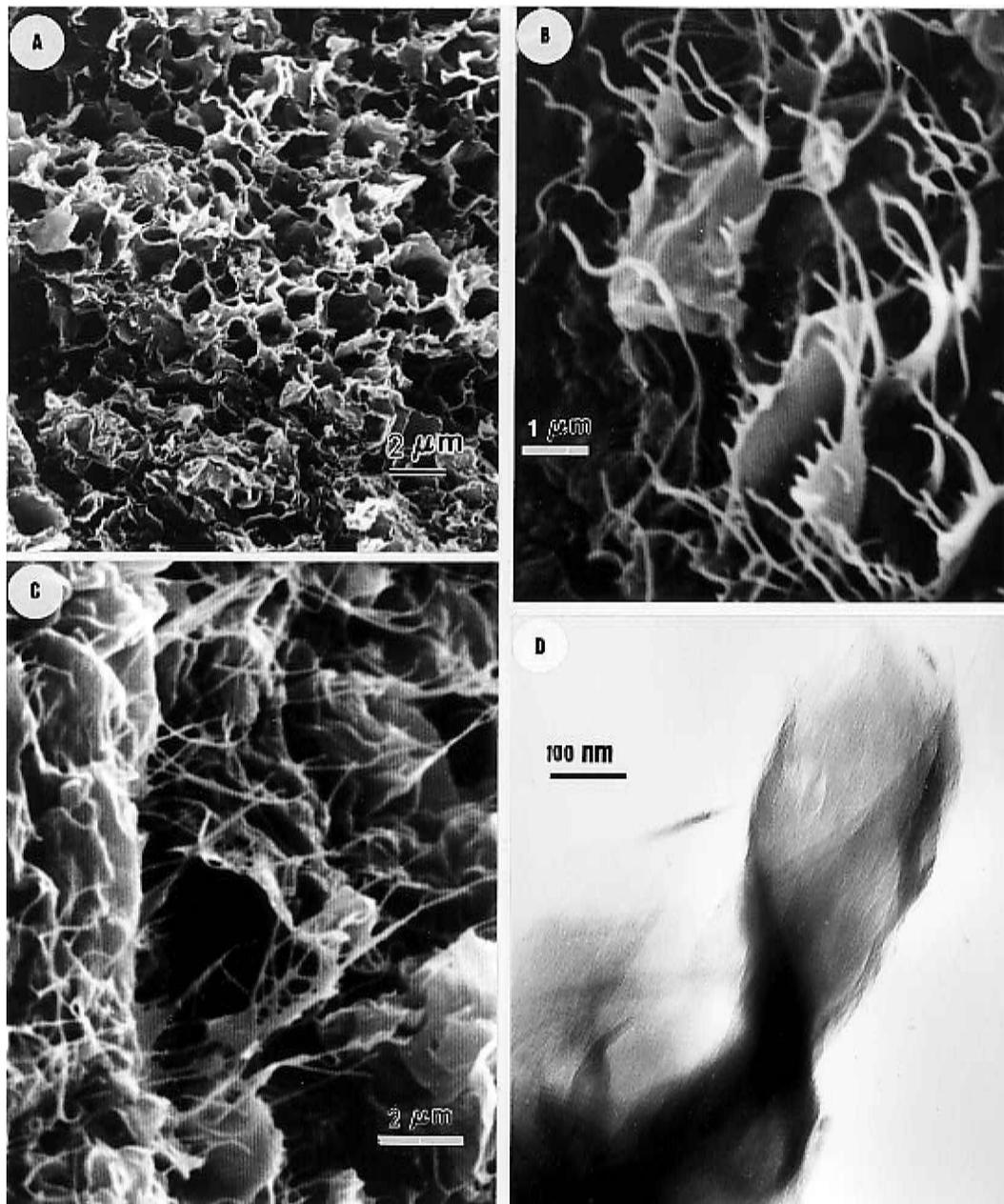

FIG. 3. (A) Cornflake microstructure. (B) Short filaments originating from smectite particles as observed by SEM. (C) Longer filaments connecting smectite particles by forming a cobweb, observed by SEM. (D) TEM photograph of a curl formed at the edge of a smectite particle.

and irregularly shaped flakes. These flakes show a tendency to be connected forming flocs or aggregate structures separated by voids of varying sizes and shapes. Such laminar aggregates are often associated with fibrous edge morphologies (Fig. 3B and 3C), probably of neoformational origin by the curling of laminar particles of smectite at their edges as seen by TEM observation (Fig. 3D). This agrees with the theory of Vedeneeva Tsukerman (1957) who suggested that they appear as rolled-up edges of extremely thin films formed as the result of edge-to-edge aggregation of particles.

In a much smaller amount, illite particles have been observed as platy-like particles corresponding to relatively thick and well developed illite crystals which are thought to be the remains of the original rock.

Furthermore, ribbon-like particles formed by interwoven fibres curled at their edges (Fig. 4A, 4B and 4C) have been found covering pore walls in large size voids and fractures. In these areas, variable Si, Al, Mg, Fe, Ca and K contents (always present) were detected by EDS. Although previous authors (Güven *et al.*, 1980; Keller *et al.,* 1986) described similar lath-shaped morphologies as illite, we cannot rely on the morphology to define the mineralogical nature because EDS results are qualitative and it is not possible to define the quantitative composition. There is, therefore, a reasonable doubt about what kind of mineral corresponds to this particular morphology.

TEM

The TEM micrographs revealed the coexistence of pure smectite, pure illite and interstratified I-S. As the method of sample preparation preserves the texture of the rock, smectite layers have not collapsed and can be distinguished from illite layers by their appearance under TEM.

Smectite occurs over extensive areas surrounding remains of illite particles (Fig. 5A). Smectite particles show anastomosing and imperfect 14 Å lattice fringe images with typical changes in image contrast along the layers, due to small orientation changes in the crystal (Bandfield & Eggleton, 1988) and a high density of dislocations.

Illite particles show straight and relatively defect-free lattice fringes, with continuous and constant 10 Å interlayer spacings. Image contrast does not change along an individual fringe. Usually, illite particles exhibit a characteristic mottled contrast (Fig. 5A), which is due to lattice strain, which, in turn, is due, at least partially, to cation diffusion induced by the electron beam. This mineral occurs as thin packets within a matrix of smectite. The illite particles usually appear isolated and surrounded by extensive areas of smectitic nature. Studying these particles in more detail it is possible to observe within them a physical breakdown process which can be interpreted as an exfoliation or microdivision perpendicular to the stacking direction (Fig. 5B).

Mixed-layer I-S minerals have also been found, some being R = 1 and showing basal spacings corresponding alternatively to illite (10 Å) and smectite (14 Å) (Fig. 6B).

The study of the textural relationships between particles allowed the analysis of the transformation process from illite to smectite in all its stages. It is possible to order the sequence through which illite particles undergo weathering generating smectite particles in a solid-state process.

Initially, some crystal planes gradually open from 10 Å (illite-like layer) to 14 Å (smectite-like layer) interlayer spacing. This structural modification involves the replacement of K^+ by hydrated interlayer cations and a slight reorganization of the 2:1 layer structure (Banfield & Eggleton, 1988). Then, a disarticulation process along the smectite-like layer (more weakly bonded) (Ahn & Peacor, 1986b) results in thinner crystal units with multiples of 10 Å thickness. These units evolve by disconnecting from the parent crystal as the cleavage process advances. The cleavage front is often noticeable by a sharp edge corner (Romero *et al.*, 1992) (Fig. 5C).

A more advanced stage in the weathering process consists of the total separation of illitic units along layer planes (Fig. 4D). These fragments of the initial crystal still preserve their illitic entity (the general interlaminar spacing is 10 Å along them). Diffuse non-layered matter can be observed within the voids between them. Romero *et al.* (1992) consider that this 'amorphous' phase (gel) has its origin in the dissolution of illite particles.

Also mixed-layer I-S has been found as an intermediate product of this alteration process. The basal spacings are due to a regular arrangement of illite and smectite layers (R = 1) (Fig. 6B). This type of interstratified mineral in similar weathering processes in phyllosilicates has been found by other authors (Klimentidis, 1986; Veblen *et al.,* 1990).

Finally, the genesis of smectite from illite particles is produced by the relative loss of K^+ and Al^{3+} and increase in the Si^{4+} and Mg^{2+} content which can

come from external sources in the same basin. Aoudjit *et al.* (1995) suggested that the neoformation of smectite under hydromorphic conditions is considered to be a common process and is explained by the very high contents of silica and basic cations which favour the formation of smectite.

From a structural point of view, the phyllosilicate structure of micas favours the formation of smectite
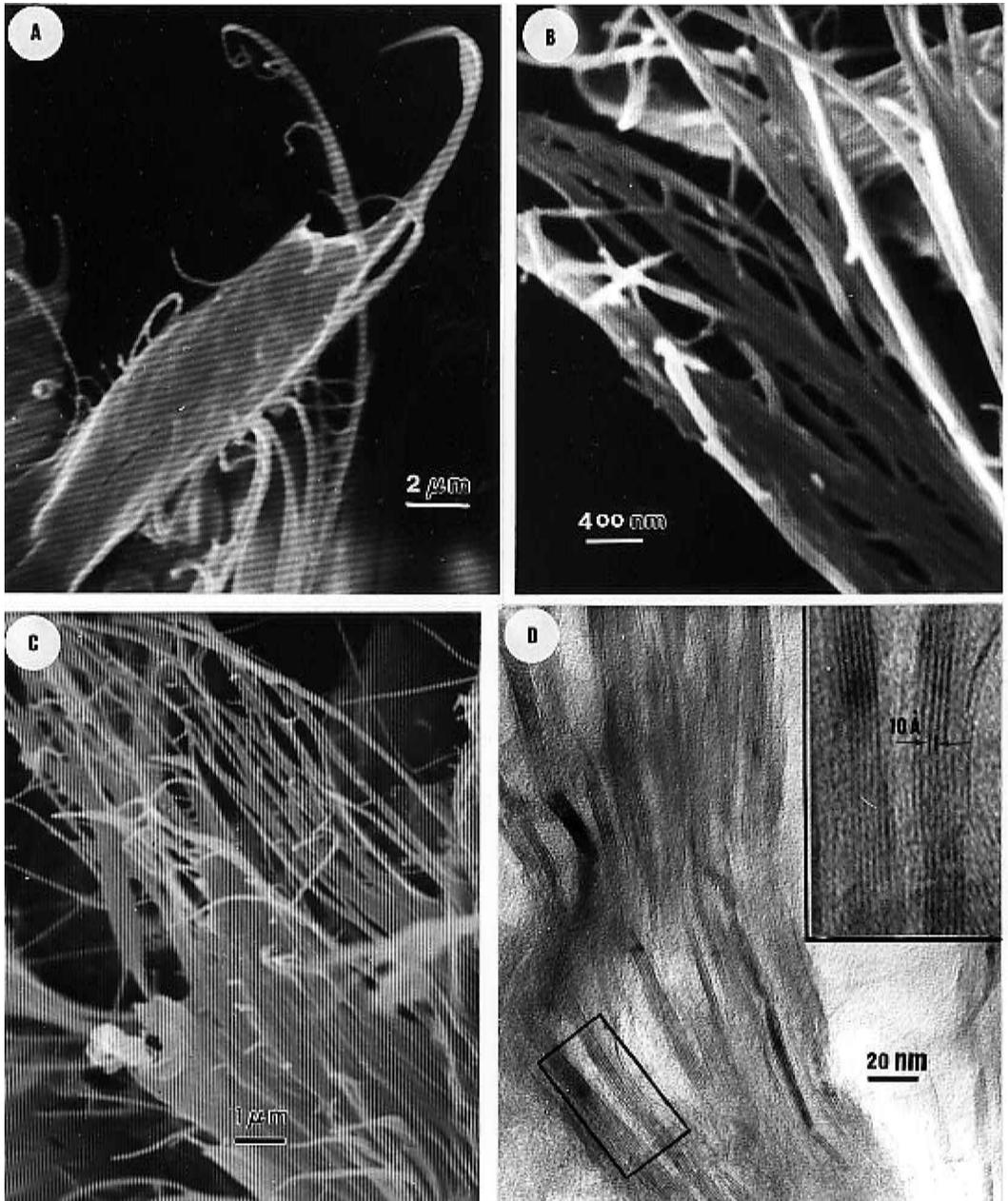

FIG. 4. (A, B, C) Ribbon-like particles formed by long interweaved filaments. (D) TEM image from an aggregate of elongate illite particles. The magnified view allows measurement of the 10 Å interlayer spacing.
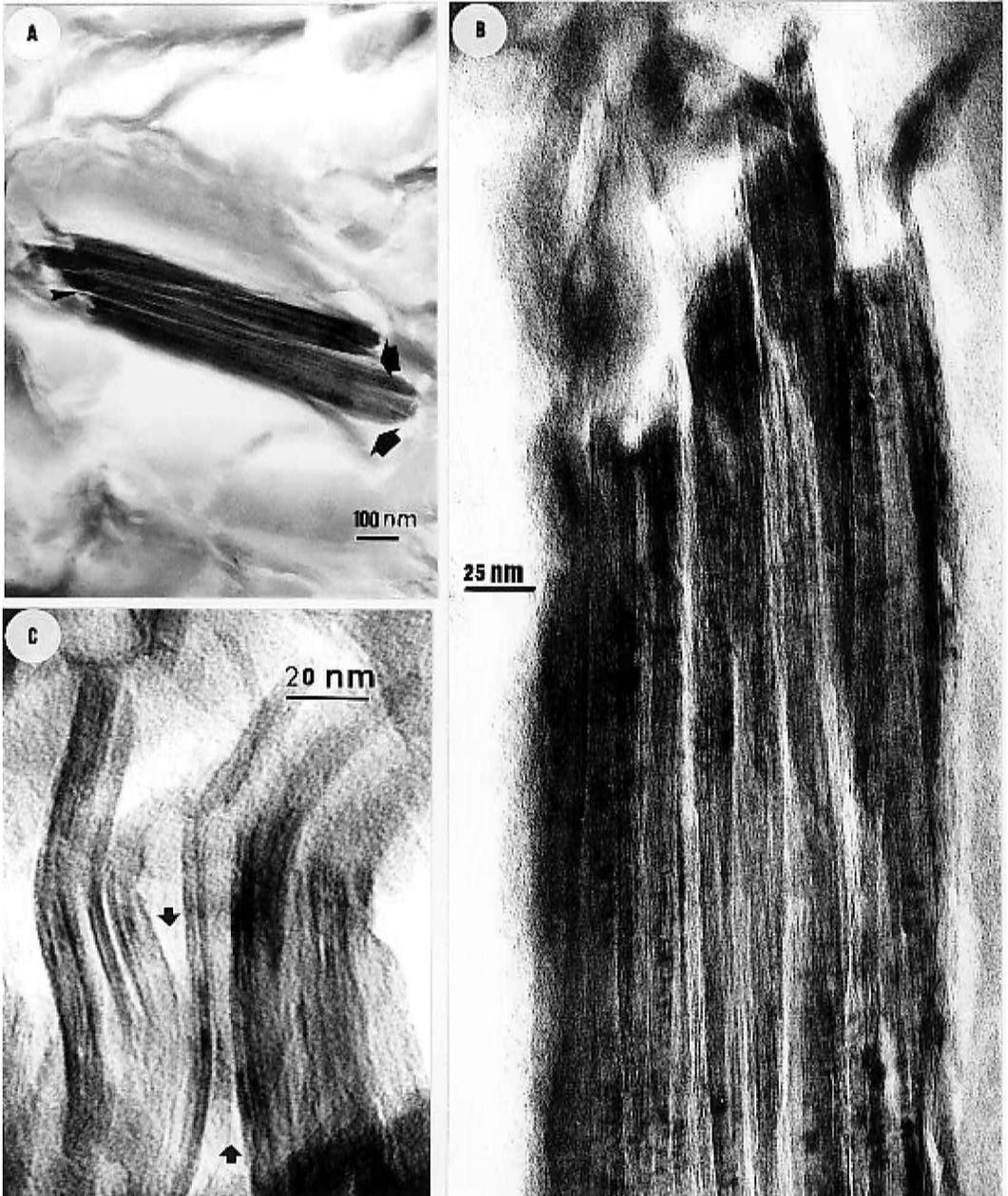
FIG. 5. (A) TEM micrograph of an illite particle. (B) Magnified view from the edge of the illite particle. Exfoliation planes along which the particle breaks down can be observed. (C) A more developed stage in the alteration process. The cleavage front can be recognized by a sharp edge corner indicated by the arrow.

(Aoudjit *et al.*, 1995) because it consists only of the opening of the interlaminar spacing with slight reorganization of the 2:1 layer structure.

Consequently, there are remains of illite particles (straight and relatively defect-free lines) surrounded by extensive areas of smectite (imperfect and wavy
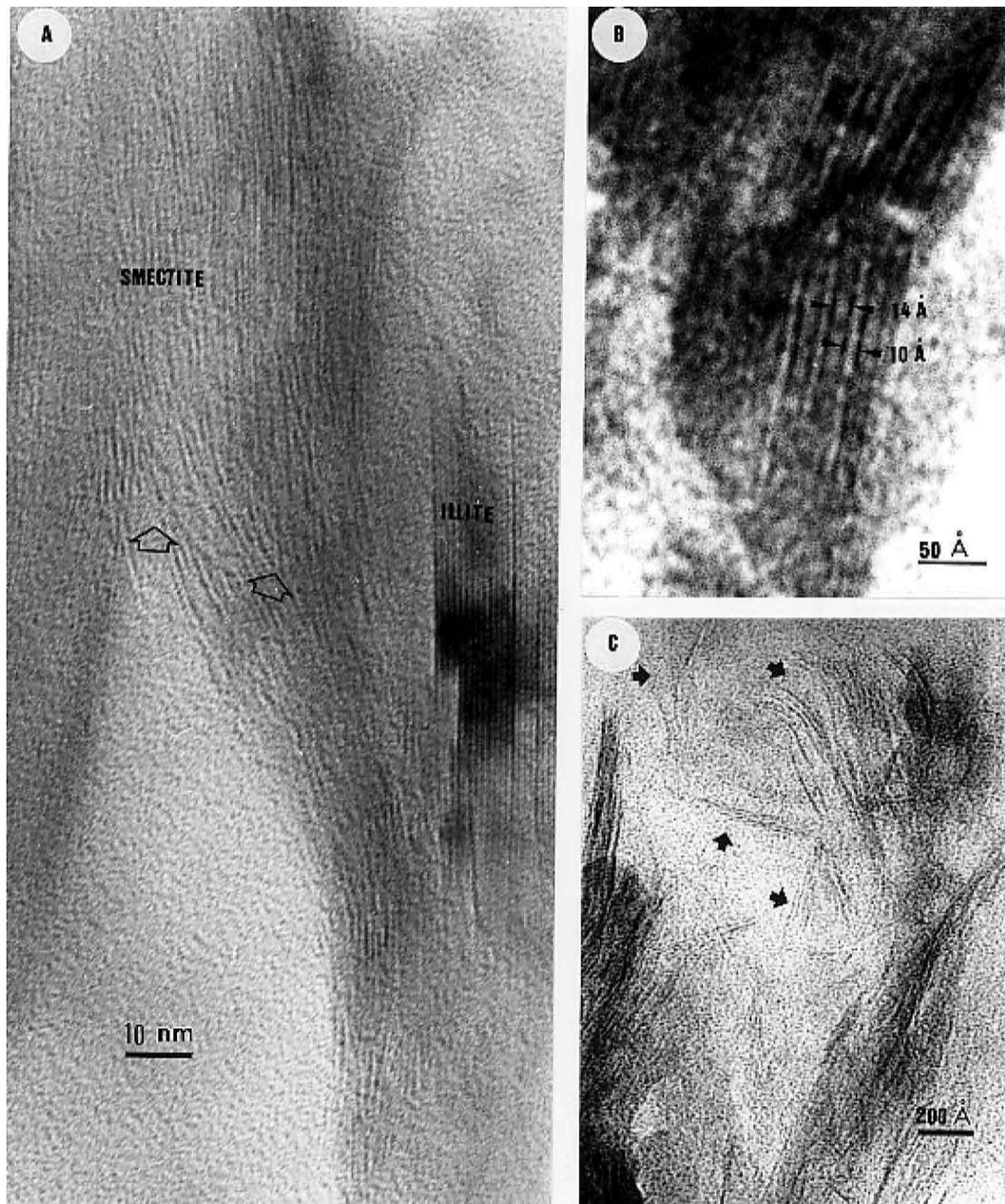
FIG. 6. (A) Remains of illite particles surrounded by extensive areas of smectite. Arrows show edge dislocations in smectite particles. (B) Mixed-layer illite-smectite ($R = 1$) as an intermediate product in the alteration process. (C) The total destruction of the illite structure results in the individualization of monolayers (arrows) and the formation of a colloidal phase.

fringes) with a high density of edge dislocations which may serve as diffusion pathways (Ahn Peacor, 1986a) (Fig. 6A). This type of dislocation has been described by Bell (1986) as non-conservative boundaries where terminating and bifurcating lattice planes of various types form the boundary between

illite and smectite layers. In this study, they have been found between smectite particles.

An extreme case of breaking off is the total destruction of the illite particles and the individualization of monolayers (Fig. 6C). Romero *et al.* (1992) and Kittrick (1973) suggested that the monolayer organization can be considered as the limiting stage for solid-state degradation of 2:1 phyllosilicates. This colloidal phase is the raw material in the solid-state formation of smectite particles. The next stage, if the process goes on, is the total dissolution of the illite structure to form a multielementary gel from which secondary minerals will be formed (Aoudjit *et al.*, 1996). In any case, it is not always necessary to go through these latter stages in the transformation and genesis of smectite.

CONCLUSIONS

The bentonites from the Green Clays Unit of the Tagus basin essentially originated by neoformation. However, small amounts of detrital dioctahedral illite became unstable in a Mg-rich environment and underwent a weathering process forming smectite. The transformation involves a charge decrease which is achieved by the loss of interlayer cations with a slight change in the tetrahedral sheet (Robert, 1972). In this way, crystals are gradually split into thinner units which evolve by disconnecting from the parent crystal. Meanwhile, an increase in the Mg content (very abundant in the basin) takes place in the particles. Different compositions of illite, mixed-layer I-S and smectite were analysed in a way similar to the different stages in the weathering of the illite by opening of the layers. Furthermore, a colloidal phase (isolated monolayers) was found around particles as a by-product of the extreme disarticulation of the illite structure (Romero *et al.*, 1992). This colloidal phase could be the raw material for the solid-state formation of smectite. The process could continue with the dissolution and formation of a multi-elementary gel phase (Aoudjit *et al.*, 1996) and later crystallization of secondary minerals. These weathering and transformation processes take place at the same time as the neoformation of different types of filamentous morphologies.

ACKNOWLEDGMENTS

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