# RANDOMLY INTERSTRATIFIED KAOLINITE–SMECTITE FROM GALICIA (NW SPAIN): A NEW PROCEDURE FOR DETERMINATION

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**Abstract**—A new protocol was developed to examine an assemblage of kaolinite–smectite in a buried horizon of a paleosol developed on gabbro parent material. The new extraction procedure appears suitable for removing kaolinite and for ascertaining the nature of the smectite interstratified with kaolinite. Smectite was identified by X-ray diffraction (XRD) and infrared (IR) patterns, cation exchange capacity (CEC) and chemical analyses.

The results obtained provide for increased understanding of the process of transformation of smectite into kaolinite.

**Key Words**—Acid Soil, Gabbro, Interstratified Kaolinite-Smectite, Paleohorizons.

## INTRODUCTION

Interstratification among 2:1 or 2:2 clay minerals is rather frequent in soils. Relatively less usual are interstratifications that include 1:1 phyllosilicates of the kaolinitic type (Sawhney 1989). Nevertheless, examples of interstratifications of kaolinite with a 2:1 mineral of the smectite type have been reported; however, only 1 case of kaolinite–vermiculite interstratification was found (Wada and Kakuto 1983).

Sudo and Hayashi (1956) were the first to describe a kaolinite–smectite interstratified in an acid clay deposit in Japan. Later, Altschuler et al. (1963), Wiewióra (1971) and Wilson and Cradwick (1972) reported similar interstratifications in soils of Florida, Poland and Scotland, respectively. In the last 2 decades, this interstratification has been observed in a soil of Burundi (Herbillon et al. 1981), in one from El Salvador (Yerima et al. 1985) and in an Indian saprolite (Pal et al. 1989). In all of these cases, the soils studied were developed on basic igneous rocks. In their review, Norrish and Pickering (1983) stated that 40 profiles formed from basic rocks contained the interstratified kaolinite–smectite as the only clay mineral. However, kaolinite–smectite interstratified has also been found in association with limestone (Shultz et al. 1971; Robinson and Wright 1987) and in hydrothermal deposits in Kamchatka by Sahkarov and Drits (1973), in Poland by Wiewióra (1973) and in Spain by Cuadros et al. (1994).

Despite these occurrences, detectability of this interlayer mineral is difficult. The identification is based on shifts of the interlayer diffractometric peak upon various treatments. In this paper, we propose a new procedure that improves the recognition of the interstratified kaolinite–smectite.

When recognized, these mixed-layer minerals are referred to as an interstratification between kaolinite and a mineral belonging to the family of smectites. Furthermore, the interstratified kaolinite–smectite is considered intermediate in the transformation of 2:1 expandable minerals into 1:1 minerals through progressive aluminization of the 2:1 mineral interlayers (Kukovsky 1969; Karathanasis and Hajek 1983; Wada and Kakuto 1983).

The aims of this work are 1) to demonstrate the smectitic nature of a 2:1 mineral interstratified with kaolinite found in the buried horizons of polygenetic, acid, well-drained soils formed on gabbro parent material in Galicia (NW Spain); 2) to propose a new procedure that improves the identification of the 2:1 mineral when, as in our case, it is poorly detectable within the interstratified mineral; and 3) to speculate about the transformation of a 2:1 mineral into a 1:1 structure.

## SITE DESCRIPTION

Samples were collected in the province of A Coruña, at the second km of the Monte Castelo-A Silva road (geographic position 43°6'40"N, 8°40'34"W). The profile PT1, which is known as "Poste Telefono", was sampled. In the same area, another profile, PT2, was sampled. Both PT1 and PT2 profiles consist of a modern soil, an Andisol (García-Rodeja et al. 1987), that rests on a buried soil. Two sections opened about 1.5 km away from this site displayed a similar buried profile that has been classified as a Tropept (Macías Vázquez et al. 1978). The description of profile PT1 is in Table 1.

## MATERIALS AND METHODS

The samples were collected from buried profiles in the 2 soils. In both cases, they are constituted by the horizons 2Bwb1, 2Bwb2 and 2Cb. These horizons had a silty clay loam texture and an acid reaction (pH from 4.60 to 4.54).

Table 1. Descriptions of the profile PT1, "Poste Telefono". A Coruña province, Galicia (Spain).

Climate: wet oceanic; mean annual precipitation: 1600 mm; mean annual air temperature: 11 °C; geographic position: 43°6'40"N, 8°40'34"W; elevation: 400 m a.s.l.; exposure: S; slope: about 5%; parent material: gabbro; vegetation: *Ulex europaeus, Erica cinerea, Calluna vulgaris, Daboecia cantabrica, Pteridium aquilinum*; soil: Alic Fulvudand (Soil Survey Staff 1996).

| | Depth (cm) | Munsell color | Tex-ture† | Stucture‡ (USDA) | Consistency§ | Plasti-city¶ | Pores# | Bound-ary†† | Observations‡‡ |
|---|---|---|---|---|---|---|---|---|---|
| A | 0–22 | 2.5YR2/4 | cl | 2f-m cr | mfr-fi; wss | wsp | 3mi&vf&f&m&co | gs | rf with Mn coa |
| BA | 22–38 | 5YR3/3.5 | l | 2f-m cr | mfr-fi; wss | wsp | 3mi&vf&f, 2m&co | gs | rf with Mn coa |
| Bw | 38–60 | 5YR3/3 | l | 2m sbk | mfi; wss | wp | 2mi&vf&f, 1m&co | gs | rf with Mn coa |
| 2Bwb1 | 60–110 | 7.5YR7/6 | l | 2m sbk | mvfi; ws | wp | 2mi&vf&f, 1m, v1co | gs | Fe & Mn nod |
| 2Bwb2 | 110–140 | 7.5YR7/6 | l | 2m-co sbk | mvfi; ws | wp | 1mi&vf&f, v1m | gs | Fe & Mn nod |
| 2Cb | 140–185+ | 7.5YR5/8 5YR5/8 5YR5/6 | | saprolite | | | 1mi&vf | | Fe & Mn nod |

† c = clay, l = loam.
‡ 2 = moderate; f = fine, m = medium, co = coarse; cr = crumb, sbk = subangular blocky.
§ m = moist, w = wet; fr = friable, fi = firm, vfi = very firm; ss = slightly sticky, s = sticky.
¶ w = wet; sp = slightly plastic, p = plastic.
# v1 = very few, 1 = few, 2 = common, 3 = many; mi = micro, vf = very fine, f = fine, m = medium, co = coarse.
†† g = gradual; s = smooth.
‡‡ rf = rock fragments; coa = coatings; nod = nodules.

Here, for brevity, we present data obtained from the 2Bwb2 horizon of pit PT1, which contains the largest amount of the interstratified material. The other 2 buried horizons of PT1 and the buried horizons of PT2 have chemical and physical characteristics similar to those of the other 2 sections at 1.5 km (Macías Vázquez et al. 1978; Corti and Fernandez Sanjurjo 1993).

Samples were air-dried and sieved through a 2-mm sieve and were treated with NaClO solution adjusted at pH 8.8 to remove organic matter (Lavkulich and Wiens 1970); the organic-free sample was deferrated by citrate-bicarbonate-dithionate (CBD) (Mehra and Jackson 1960). The Na-saturated sample was sieved at 53 μm to remove the sand and then was submitted to sequential sedimentations to separate the clay size fraction (<2 μm). The clay suspension was sonicated, further deferrated with CBD, washed and dialyzed until soluble Na was not detected.

The clay was treated with 1 *N* NaF solution (solid: liquid ratio 1:50 w:v) at ambient temperature and boiled for different lengths of times (30, 60, 90, 120 and 240 min).

For the purpose of investigating the nature of the 2:1 mineral present in the interstratified component, a new procedure for dissolving kaolinite was followed. Aliquots of Na-clay were heated at 550 °C and successively boiled twice (5 min each) in 1 *N* NaF solution (solid: liquid ratio 1:50 w:v). To show the effect of this procedure on the removal of hydroxy-Al polymers from the interlayer of the 2:1 mineral, the clays were subsequently K-saturated and heated at 300 °C for 1 h. To assess the expandability of this mineral, an aliquot of the clay treated with the above procedure was Mg-saturated and solvated with glycerol. XRD analyses were performed with a Philips PW 1710 diffractometer using the Fe-filtered Co-$K\alpha_1$ radiation at

35 kV and 25 mA, step size of 0.01 °2θ and counting time of 1 s.

IR spectrometric analysis was done using a Perkin Elmer FTIR 1710 apparatus on the clay fraction.

CEC was determined by saturation of the samples with 1 *N* MgCl$_2$ solution; Mg was successively replaced by Na using a 3 *N* NaNO$_3$ solution. The exchanged Mg$^{2+}$ was determined with 0.0 *N* EDTA solution buffered at pH 10 (NH$_4$Cl/NH$_4$OH) in the presence of eriochrom black T. The values reported are the average of 3 measurements.

Total elemental analysis was conducted on clay specimens by X-ray fluorescence (XRF) with a Philips PW 1410 spectrometer. From the percentage of Si and Al, the values corresponding to the impurities of quartz and gibbsite have been subtracted. The amounts of these 2 minerals were evaluated by adding known aliquots of quartz and gibbsite of clay size to the 2Bwb2 clay as internal standards.

Aliquots of clay were examined using a Philips 505 scanning electron microscope, equipped with an energy dispersive X-ray spectrometer (EDX) PV 9800.

## RESULTS

### XRD

The main features of Na-saturated clay (Figure 1) are prominent asymmetric peaks at 0.750–0.755 nm and 0.718 nm. A secondary asymmetric peak is also present at 0.357 nm. The interpretation of these diffraction lines will be further discussed. Minor diffraction lines are present at 0.484 and 0.437 nm ascribed to gibbsite and at 0.334 nm ascribed to quartz.

Air-dried K-saturated clay (Figure 2, trace a) heated at 300 °C (Figure 2, trace b) shows a wide asymmetric peak at 0.740 nm and a minor one at 0.713 nm. Mg-saturated clay (Figure 2, trace c) displays a peak at
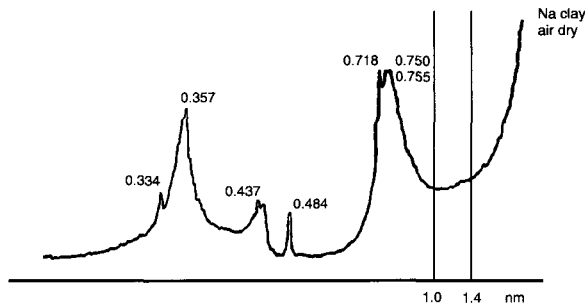
Figure 1.   XRD patterns of Na-saturated, air-dried clay sample manually compressed into Plexiglas slides (2Bwb2 clay).

0.713 nm, while the lines at 0.750–0.755 nm (Figure 1) disappear. The Mg-glycerol clay (Figure 2, trace d) shows a wide asymmetric peak at 0.740 nm with a shoulder at 0.713–0.718 nm. Heating the K-saturated sample at 550 °C for 2 h (Figure 2, trace e) results in the disappearance of the peaks and the appearance of a broad diffraction area between 0.96 and 1.40 nm. The Mg-saturated sample heated at 550 °C (Figure 2, trace f), shows a broad diffraction area (0.96 to 1.40 nm) only. The Mg-saturated specimen heated at 550 °C and then solvated with glycerol (Figure 2, trace g) shows the disappearance of all peaks.

The results obtained by the different treatments suggest that the 0.718-nm peak of the Na-saturated clay belongs to kaolinite, while the other, with a maximum at 0.750–0.755 nm, is interpreted as due to an interstratified kaolinite-2:1 mineral (Figure 1). The peak at 0.750–0.755 nm that shifts only slightly (0.740 nm) after K-saturation and heating at 300 °C, indicates that the 2:1 mineral component interstratified with kaolinite is fully collapsed. Similar results were obtained by Herbillon et al. (1981) and Yerima et al. (1985), who attributed such collapse to the presence of Al-hydroxypolymers in the interlayered position of the 2:1 mineral. The absence of collapse in the K-saturated and 300 °C heated specimen indicates absence of halloysite (Quantin et al. 1984; Delvaux et al. 1990). The similarity between the diffractograms 2c and 2d suggests that the 2:1 mineral present in the interstratified component has no swelling properties. The disappearance of all peaks and the appearance of the broad area between 0.96 and 1.40 nm after heating at 550 °C indicate that the 2:1 mineral interstratified with kaolinite contains hydroxy-Al polymers in the interlayers. Moreover, the appearance of this broad area excludes the presence of the tubular halloysite that should have a peak at 0.740 nm (Carson and Kunze 1970) and of another halloysite with a peak at 0.756 nm (Kunze and Bradley 1964). In fact, in both cases, the peaks at 0.740 and 0.756 nm should have disappeared upon heating at 550 °C. The 2:1 mineral interstratified with kaolinite, when Mg-saturated and heated at 550 °C, showed a broad diffraction band from 1.0 to 1.4 nm
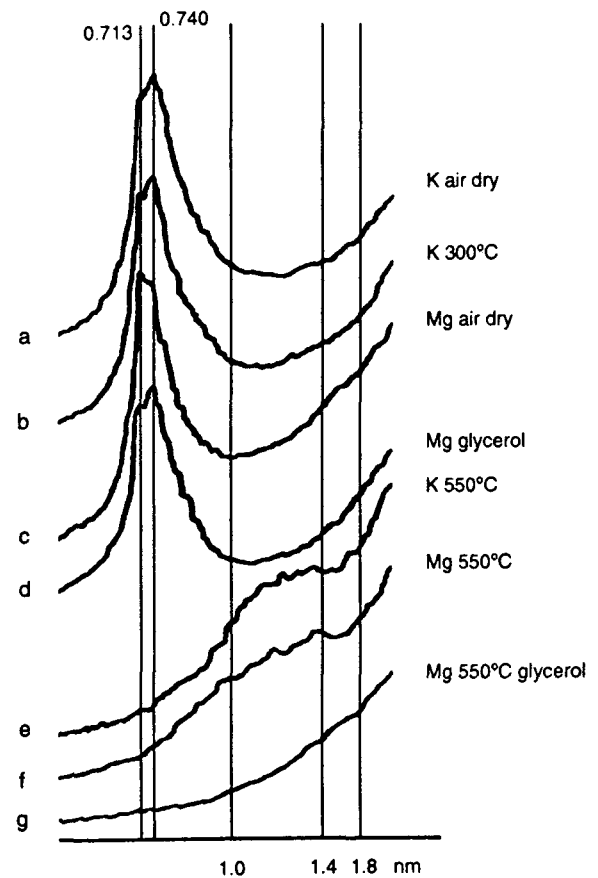


Figure 2.   XRD patterns of clay samples saturated with different ions, solvated with glycol and thermally treated.

(Figure 2, trace f); upon treatment with glycerol (Figure 2, trace g) this diffraction area disappeared, suggesting the presence of a disordered smectite. The same results were obtained with Ca-saturated and Ca-glycerol treated clay (diffractograms not shown).

Figure 3 shows the diffractograms of the clay treated with NaF. The NaF treatments, either at ambient temperature or boiled up to 120 min, were ineffective in removing the hydroxy-Al interlayers. When the sample was boiled for a longer time (240 min), the observed decrease of the peaks indicated a destruction of the interstratified component and of the kaolinite; this effect was also reported by Rich and Obenshain (1955).

Diffractograms of clay treated with NaF at ambient temperature (Figure 4), show that the interstratified component is not affected by this treatment; for example, for the K-saturated and 300 °C heated and NaF treated samples, the same peak at 0.740 nm was obtained (traces 2b and 4b, respectively). The X-ray patterns of the clay in Figure 4 (traces c, d, and e) show a peak at 0.996 nm which has been created by the removal of the kaolinite and the hydroxy-Al polymers
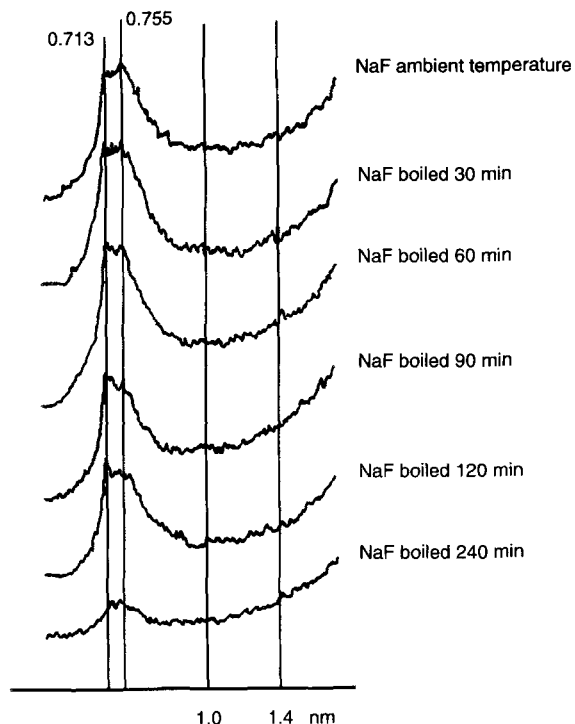
Figure 3. XRD patterns of clay samples treated with NaF at ambient temperature and boiled in NaF for different lengths of times.



Figure 4. XRD patterns of clay sample subjected to different chemical and thermal treatments.

that were present in the interstratified mineral. When Mg-saturated, the clay shows a broad diffraction area that can be attributed to a disordered 2:1 mineral (Figure 4, trace f). When this Mg-clay was solvated with glycol (Figure 4, trace g) the broad band disappeared, indicating the smectitic nature of the 2:1 mineral. The removal of the hydroxy-Al polymers from the interlayer position after a strong treatment needed to dissolve the hydroxy-Al interlayered of the smectite, suggests that the interlayers are highly polymerized.

IR Analyses

The IR analysis of the clay from the 2Bwb2 horizon (Figure 5, spectrum A) shows the adsorption bands characteristic of kaolinite (3696, 3650–3670, 3625 and 930 cm$^{-1}$) and smectite (3640 cm$^{-1}$ and a large band from 3200 to 3600 cm$^{-1}$) as observed in similar samples by Serratosa et al. (1962) and by Oinuma and Hayashi (1965). In Figure 5, the spectra D and E are obtained for Zettlitz kaolinite and for Na-montmorillonite, respectively, used as references. Similar results have been obtained by Wiewióra (1973) and by Watanabe et al. (1992) for natural occurring and by Poncelet and Brindley (1967) for artificially produced mixed layers.

Further support for the presence of smectite or smectitic material is given by Figure 5, spectrum B, which has been obtained by heating the clay at 550
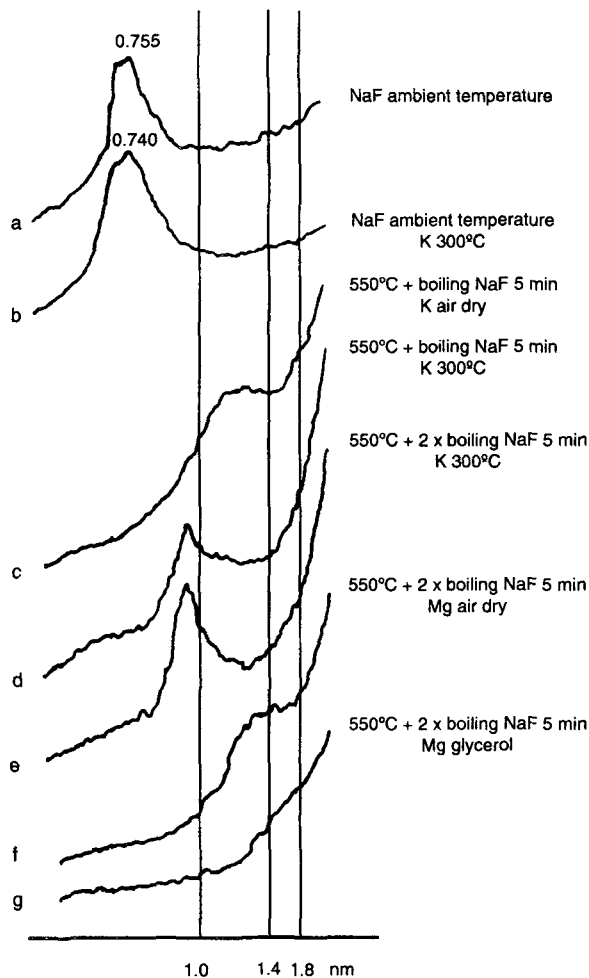
°C. This spectrum is similar to spectrum E, recorded for a standard Ca-montmorillonite. Spectrum C represents the difference between spectra A minus B and is similar to the spectrum from Zettlitz kaolinite. Evidently the mineral destroyed by heating at 550 °C is kaolinite, while the mineral that remains is oxy-Al interlayered smectite.

We cannot, however, ascribe a specific band to the oxy-Al interlayered smectite. In fact, the band at 3640 cm$^{-1}$ that approaches the area between 3600 and 3700 cm$^{-1}$ ascribed to hydroxy-Al interlayered montmorillonite (Barnhisel and Bertsch 1989) is also characteristic of montmorillonite saturated with different ions, but without Al-interlayered (Oinuma and Hayashi 1965).

CEC

The increase in CEC due to the removal of the Al-hydroxides starts after boiling the sample with NaF for 30 min (Table 2). The CEC remains virtually the same
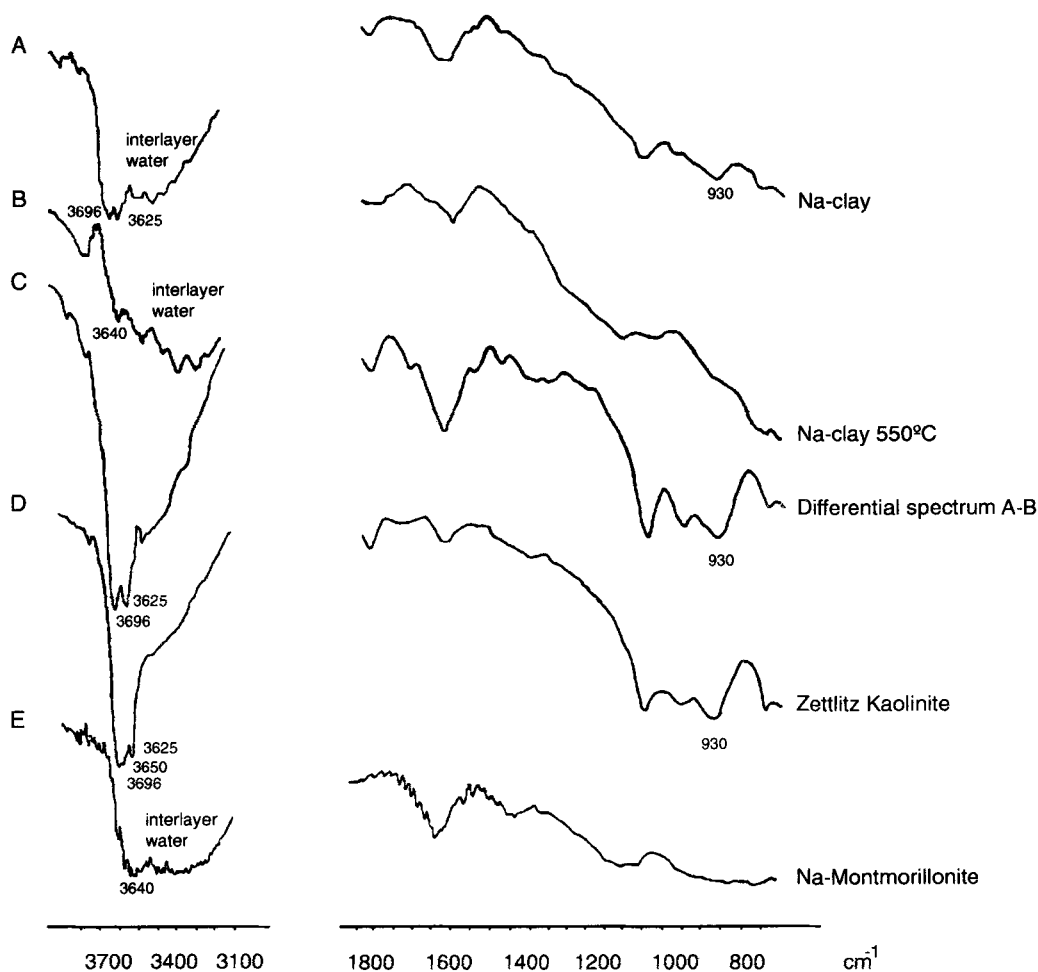
Figure 5.    IR absorption spectra of Na-clay air-dried (A), Na-clay heated at 550 °C (B), standard Zettlitz kaolinite (D) and standard Na-montmorillonite (E). The C trace is the differential spectrum between spectra A minus B.

Table 2.    CEC of the untreated Na-clay and of the clay differently treated.

| Treatments of the Na-clay | cmol(+) kg$^{-1}$ |
|---|---|
| Air-dry | 28.8 |
| NaF ambient temperature 30 min | 27.6 |
| NaF boiled 30 min | 46.5 |
| NaF boiled 60 min | 45.1 |
| NaF boiled 90 min | 47.6 |
| NaF boiled 120 min | 50.6 |
| NaF boiled 240 min | 40.4 |
| NaF boiled 300 min | 33.8 |
| 550 °C | 23.7 |
| 550 °C + boiling NaF 5 min | 40.5 |
| 550 °C + twice boiling NaF 5 min | 73.3 |
| 550 °C + twice boiling NaF 5 min + boiling NaF 60 min | 92.6 |
| 550 °C + twice boiling NaF 5 min + boiling NaF 120 min | 105.1 |

until the sample is boiled for 2 h, after which it decreases. We explain this result as due to 2 countereffects: the initial increase in CEC is due to the removal of Al-polymers and the decrease, after a 4-h treatment, is caused by the destruction of the minerals.

A confirmation of the effective removal of the hydroxy-Al interlayered and of the corresponding increase in CEC has been obtained by heating the sample at 550 °C and by boiling it in NaF. From the results obtained (Table 2) it appears that, other things being equal, the longer the boiling time in NaF, the larger the increase in CEC of the clay. A value of 105 cmol(+) kg$^{-1}$, typical for an expandable 2:1 mineral, was obtained.

Elemental Analyses

The content of hydration water (H$_2$O$^-$) of the clay is 5.25%, that of Fe$_2$O$_3$ 4.47% and that of MgO 1.17%. The amounts of SiO$_2$ and Al$_2$O$_3$ are 43.28 and 32.59%, respectively, which give a Si/Al molar ratio of 1.125.

A composition such this can be ascribed, in addition to kaolinite, to the presence of a 2:1 mineral.

## Scanning Electron Microscopy (SEM)

The SEM observations reveal a kaolinite having a size relatively small, about 0.1–0.3 μm. According to Thiry (1982) and Tessier (1984), small size kaolinites typically contain small quantities of interstratified smectite. This also means that these kaolinites generally derive from the interstratified kaolinite–smectite (Thiry and Weber 1977; Thiry 1982; Tessier 1984; Corti and Fernandez Sanjurjo 1993).
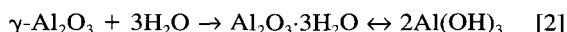
## DISCUSSION

The results obtained indicate that the sample analyzed contains, in addition to kaolinite, an interstratified kaolinite-2:1 mineral. On the basis of the position of the peak we suggest that the interstratified mineral contains approximately 10% smectite, even if some doubts still exist about its positive identification. The usual procedure, NaF treatments without heating, was ineffective in collapsing and swelling of the smectite. The method described here appears effective in removing the kaolinite present, in concentrating the remaining smectite and in rendering the NaF treatments more effective in dissolving the hydroxy-Al polymers. The successful removal of the interlayered Al is probably due to the increased effectiveness of the NaF in attacking the Al-interlayered once the kaolinite is no longer present upon heating. This in spite of the fact that the Al-polymers have been changed into Al-oxides. A possible sequence of the reactions that could have dissolved the Al-interlayer is here presented:

1) During the heating at 550 °C of the Na-saturated clay, the highly condensed hydroxy-Al polymers present in the smectite are subjected to depolymerization, detachment from the mineral structure and formation of Al-oxides. This treatment would produce the Al-oxide $\gamma$-$Al_2O_3$:

$$\text{hydroxy-Al polymers} + 550\ ^\circ\text{C} \rightarrow \gamma\text{-}Al_2O_3 \quad [1]$$
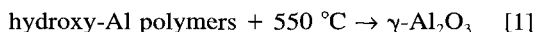
2) The resulting $\gamma$-$Al_2O_3$ adsorbs water:

$$\gamma\text{-}Al_2O_3 + 3H_2O \rightarrow Al_2O_3\cdot3H_2O \leftrightarrow 2Al(OH)_3 \quad [2]$$

3) The clay heated at 550 °C and successively boiled in NaF solution effectively removes the Al products, $Al(OH)_3$, from the interlayer according to this proposed reaction:

$$Al(OH)_3 + 6NaF \rightarrow Na_3AlF_6 + 3Na^+ + 3OH^- \quad [3]$$

This proposed mechanism seems to be supported by the rise in pH obtained after the NaF treatment. The pH of the Na-saturated clay before heating was 8.1 and the pH of the 1 $N$ NaF solution was 7.3, while that of the suspension of the heated clay in NaF solution was 9.6.

In soils, a single layer of a 2:1 mineral can produce 2 layers of a 1:1 mineral. A number of mechanisms have been proposed for the transformation of 2:1 clay minerals into 1:1. These mechanisms involve solubilization and removal of the Si tetrahedral sheet (Kukovsky 1969), as well as structural rearrangements associated with dissolution and precipitation processes (Altschuler et al. 1963; Karathanasis and Hajek 1983; Watanabe et al. 1992). The importance of hydroxy-Al interlayering in 2:1 expandable minerals in the transformation into 1:1 has been acknowledged by many authors (Jackson 1962; Altschuler et al. 1963; Poncelet and Brindley 1967; Rich 1968; Oberlin and Couty 1970; Karathanasis and Hajek 1983). In our particular case, the hydroxy-Al interlayered appears to be instrumental for the formation of the kaolinite. For this evolution of the 2:1 into 1:1 mineral, we invoke the same mechanism proposed by Wada and Kakuto (1983) for the transformation of vermiculite into kaolinite.

## CONCLUSIONS

The results indicate that the 2Bwb2 horizon in a buried soil that displays oxic properties, acquired during an ancient pedogenesis, contains interstratified kaolinite-smectite. We estimate the content of smectite at approximately 10%. The identification of the interstratified kaolinite–smectite has been obtained by a new procedure where samples are heated at 550 °C and boiled with NaF to remove the kaolinite and hydroxy-Al polymers.

We further hypothesize that the hydroxy-Al polymers in 2:1 expandable minerals occur in the transformation sequence: smectite → hydroxy-Al interlayered smectite → kaolinite.

## ACKNOWLEDGMENTS

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