Occurrence of Palygorskite in Soils of Ecija (Spain)

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Abstract

Palygorskite has been characterized in soils classified as typic argixerolls, located in an extensive Quaternary zone in the north of Seville (Spain), where the geological and climatic conditions suggest its genesis. The soils contain a Ck horizon which has different textural characteristics to the other horizons in the profiles. The presence of large white calcareous nodules and cristobalite is the principal difference between them.

The formation of palygorskite at textural discontinuities is in agreement with the characteristics of these soils. Under the present conditions of the soils (pH, magnesium and silicon concentration and soluble salts), the alteration of palygorskite to smectite is suggested.

The sporadic nucleation of large fibres of palygorskite on silica crystal suggests that this latter mineral could provide the necessary silicon for palygorskite formation.

Introduction

Palygorskite is widely distributed in many arid and semi-arid soils and sediments. Although some years ago palygorskite was considered a relatively rare mineral in soils, recently an increasing number of reports of its occurrence in soils have appeared (Zelazny and Calhoun 1977; Singer and Galan 1984).

Palygorskite has been reported in soils from many countries in the Near and Middle East, from northern and southern Africa, North and Central America, Australia and even Europe. Spain has the world's currently known reserves of sepiolite-palygorskite minerals. Their genesis has been studied by various authors (Galan and Castillo 1984; Galan 1987; Leguey *et al.* 1984; Lopez Galindo 1987; Ruiz Cruz *et al.* 1988). However, the occurrence of palygorskite in Spanish soils is relatively scarce (Sanchez Camazano and Garcia Rodriguez 1971; Sanchez Camazano *et al.* 1984). Palygorskite has been considered a relatively rare mineral as it is rarely a dominant mineral in soils and its identification is principally made by X-ray diffraction. The major X-ray reflection used for the identification of palygorskite is likely to be masked by that of illite (both minerals normally appear in soil together). Many of the reports on palygorskite consider that this mineral has been derived from the sedimentary parent material and, due to its rapid weathering, is eliminated from soil profiles, being found in soils only under arid conditions. However, in many other soils there is no evidence for palygorskite having been inherited

from the parent material, and it has been suggested that palygorskite had formed in the soil environment (Elprince *et al.* 1979; Singer 1984).

Singer (1984) considered that palygorskite formed '*in situ*' can commonly be associated with one of the three following situations: (a) modern soils affected by rising ground water; (b) soil formations with textural discontinuities; or (c) pedogenic features, such as calcretes, crusts and caliches.

In many soils, a palygorskite-smectite relationship has been observed, and the transformation of one into the other has been discussed (Abtahi 1977; Yaalon and Wieder 1976; Elprince *et al.* 1979; Bigham *et al.* 1980; Lee *et al.* 1983; MacKenzie *et al.* 1984; Shadfan *et al.* 1985). Recently, Martin de Vidales *et al.* (1987) have suggested a pedogenic model in which palygorskite is produced by smectite weathering.

Table 1. Soil description (profile I)

Soil profile location: Ecija (Seville). Finca Alcorrin (Alcorrin Estate); Km. 2 Marchena road

Horizon	Depth (cm)	Description
Ap	0-30	Dark reddish brown (5YR3/4); sandy loam; moderate to strong, thick to very thick, crumb structure; friable; porous; permeable, calcareous; moderately organic; a few roots, medium biological activity; some calcareous concretions and gravels; diffuse and smooth boundary
AB	30-60	Reddish brown (5YR4/4); clay; moderate thick subangular blocky structure; firm; slightly porous; permeable; calcareous; slightly organic; little dense; small roots; fair biological activity, some small calcareous concretions and gravels; gradual and smooth boundary
Bk	60-80	Yellowish red (5YR5/6); sandy loam, moderate medium to thick subangular blocky structure; firm to friable; slightly porous; permeable; very calcareous; diffuse and smooth boundary
Ck	80-140	Reddish yellow (5YR6/6); sandy clay loam; moderate medium to thick subangular blocky structure; friable to firm; slightly porous; very calcareous; large white and hard calcareous nodules

Table 2. Particle size distribution and organic composition of the soil
Values are expressed as percentages; OM organic matter

Horizon	Depth (cm)	Coarse sand 2000-200 μ m	Fine sand 200-20 μ m	Silt 20-2 μ m	Clay <2 μ m	OM	N	C/N	CaCO ₃
Ap	0-30	4.30	72.60	6.90	13.80	2.28	0.13	10.10	5.70
AB	30-60	10.60	20.10	11.80	55.90	1.57	0.08	12.10	15.50
Bk	60-80	4.90	72.80	4.70	15.80	0.72	0.03	14.00	64.20
Ck	80-140	5.40	56.70	3.20	33.80	0.33	0.01	19.00	62.70

Table 3. Soil pH and exchangeable cations

Horizon	Depth (cm)	pH	H ₂ O	KCl	Exchang. bases (cmol(+) kg ⁻¹)			Effective CEC ^A (cmol(+) kg ⁻¹)	CEC ^B (cmol(+) kg ⁻¹)	Base sat. (%)
					Ca	Mg	K			
Ap	0-30	7.60	7.60	6.80	35.08	3.00	1.10	39.18	39.18	100.00
AB	30-60	7.60	7.60	6.90	27.17	3.80	0.54	31.51	31.51	100.00
Bk	60-80	7.70	7.70	6.90	13.50	2.00	0.22	15.72	15.72	100.00
Ck	80-140	7.60	7.60	7.00	10.33	2.10	0.12	12.55	12.55	100.00

^A The sum of Ca, Mg and K.

^B CEC determined by compulsive exchange.

Table 4. Soluble salts and total SO₄²⁻ from the Ck horizon

Values are expressed as cmol(+) kg⁻¹

Cl ⁻	SO ₄ ²⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Total SO ₄ ²⁻
0-30	0.25	0.11	0.03	1.75	0.18	0.51

The aims of this study are: (a) to characterize palygorskite in an extensive Quaternary zone located in Ecija (in the north of Seville Province), where the geological, residual lagoon and climatic conditions suggest its genesis; (b) to follow the weathering sequences of this mineral; and (c) to provide further information on the environmental conditions of palygorskite in soils and sediments in order to gain a better pedogenic knowledge.

Materials and Methods

Soils and Location

The soils used in this study are located near the city of Ecija in western Andalucia (Spain), on the Ecija-Marchena road. Rocks ranging from Miocene (Upper Tortonian) age to the present can be distinguished in this zone (IGME 1975). Miocene landslips have deposited exogenic materials of different ages from Triassic to Upper Miocene in an olistostrome. After the most recent landslips, autochthonous sediments were deposited, including Quaternary, gravels, red clays, dark brown limestone and silt, and true caliches, in some cases due to exudation and in others from the evolution of residual lagoons, within an extensive fluvial plain. The soils studied are located on Quaternary sediments.

The description of one soil is shown in Table 1 and particle size and chemical data are given in Tables 2-4. The soils have been classified as typic argixerolls.

Methods

Soil samples were dried and sieved (<2 mm) before analysis. Particle size analysis was carried out by the chain-hydrometer method (De Leenher *et al.* 1965). The pH was measured in a soil : water suspension of 1 : 2.5 and in KCl solution. Organic matter was determined by dichromate oxidations, and extractable bases and cation exchange capacity were determined by the ammonium acetate method at pH 7.

X-ray diffraction of powdered and oriented aggregates of clay fractions, pre-saturated with Mg^{2+} , was performed with a Siemens D-500 X-ray diffractometer, using $Cu K\alpha$ radiation. Diffraction patterns of the samples were made before and after treatment with ethylene glycol and dimethylsulfoxide, K^+ -saturated and heated at 110°C. Differential thermal analysis (DTA) and thermogravimetric analysis (TG) were made in a Rigaku PTC-10A apparatus, using 40 mg of sample and a heating rate of 12°C min⁻¹.

The chemical compositions were determined after dissolving the samples in HF, HNO₃ and HCl in a Perkin-Elmer digestion bomb. The determination of Si, Al, Fe, Mg and Ca was made by atomic absorption, and Na and K by flame emission.

The scanning electron microscopy study was made with an ISI apparatus, model SS40, and the dispersion energy of X-rays was measured by a Kevex analyser, model 800. The transmission electron microscopy study was made with a Hitachi H800-2 apparatus.

Amorphous aluminosilicates were determined by extraction with 0.5 M KOH (Jackson 1969).

Results

The soils contain a Ck horizon (FAO 1988) which has different textural characteristics to the other horizons in the profiles. The presence of large white calcareous nodules in the Ck horizon is the principal difference between it and the other horizons.

The clay mineralogies of Ap, AB and Bk horizons (as deduced by X-ray) are similar to one another (Fig. 1). The dominant mineral is illite, with appreciable amounts of kaolin, smectite in low proportion (though increasing down the profile), and some quartz. The shoulder towards smaller angles of the diffraction at 9.98 Å is due to alteration of the illite. Electron microscopy confirmed that no other minerals were present.

The clay fractions of Ck horizons have different mineralogical compositions to those of the other horizons. The X-ray diffraction patterns of Ck horizons

from two different profiles are shown in Fig. 2. In the Mg-saturated sample, these horizons show a very strong reflection at $14.4 \text{ \AA}$ that swells with ethylene glycol up to $17.65 \text{ \AA}$, and collapses at $10.04 \text{ \AA}$ after potassium saturation and heating at 110°C . This reflection corresponds to smectite. There are also reflections at $10.35 \text{ \AA}$ and (one of less intensity at) $6.36 \text{ \AA}$, corresponding to 110

Fig. 1. X-ray diffraction pattern of clay fractions from Ap, AB and Bk horizons from profile I. The wavelength of each peak is given in units of $\text{\AA}$.

Fig. 2. X-ray diffraction patterns of Ck horizons from (A) profile I and (B) another profile in the same zone with similar characteristics. The wavelength of each peak is given in units of $\text{\AA}$.

and 200 reflections of palygorskite respectively. Other characteristic reflections of the same mineral also appear at 5.40 Å (130), 4.43 Å (040), 3.18 Å (400) and 2.56 Å (440). Reflections at 7.13 Å that swell to 11.18 Å after solvation with dimethylsulfoxide, and 10.04 Å (with less intensity than at 10.35 Å) are attributed to kaolinite and illite respectively. Other reflections from these minerals are also present. Cristobalite is also shown, with a diffraction at 4.05 Å.

Quartz is probably also present, as the diffraction at 3.34 Å is very strong in relation to that at 10.04 Å. (The diffraction of quartz at 4.24 Å is masked by the other diffractions.)

Fig. 3. Thermal analysis of a clay fraction from the Ck horizon from profile I.

The DTA curve from the clay fraction of the Ck horizon (Fig. 3, curve A) shows an intense endothermic effect due to initial dehydration, with a maximum at about 150°C. This effect takes place in two stages at 140 and 155°C. The TG curve shows only one weight loss (curve B), but its derivative also shows two stages (curve C). Each stage corresponds to a different dehydration that may be attributed to smectite, although the second stage appears at a slightly lower temperature, and is somewhat more intense, than that given in the literature for this mixture (MacKenzie 1970). This could also be attributed to a mixture of minerals such as smectite and palygorskite; Pérez-Rodríguez (unpublished data) has found in mixtures of sepiolite-stevensite that the first endothermic effect at about 150°C has two stages corresponding to sepiolite and stevensite respectively.

The DTA curve (Fig. 3, curve A) shows an endothermic peak at about 285°C, which is attributed to loss of coordinated water with magnesium from the palygorskite (Martín Vivaldi and Fenoll Hach-Ali 1970; Zelazny and Calhoun 1977). The other effects of the curves may be due to a mixture of the

Fig. 4. Transmission electron micrograph of clays from the Ck horizon from profile 1 ($\times 20$).

Fig. 5. Scanning electron micrograph of clays from the Ck horizon from profile 1. The longer scale marker = $1\ \mu\text{m}$.

Fig. 6. Scanning electron micrograph of calcareous nodules from profile I. The longer scale marker = $10\ \mu\text{m}$.

Fig. 7. Scanning electron micrograph of palygorskite coating quartz from profile I. Chemical analysis was by energy-dispersive X-ray of the substrate. The longer scale marker = $1\ \mu\text{m}$.

minerals shown by X-ray diffraction. The other endothermic peak between 500 and 600°C and the exothermic peak at about 900°C can be attributed to soil smectite (González García and Pérez Rodríguez 1970), and/or palygorskite. There may also be kaolinite included in these peaks.

The transmission electron micrographs showed an abundance of fibres which were assumed to be palygorskite (Fig. 4). Their proportion was higher in the $<0.2\ \mu\text{m}$ fraction than in the $0.2\text{--}2\ \mu\text{m}$ fraction. The higher concentration of palygorskite in the fine clay, rather than the coarse clay, has also been found by other authors (McLean *et al.* 1972; Shadfán and Dixon 1984; Shadfán *et al.* 1985). Scanning electron microscopy also shows the presence of fibres (Fig. 5), and chemical analysis made by X-ray dispersive energy (Si, Al, Mg) is in agreement with the chemical composition of palygorskite.

There are hard white calcareous nodules in samples of fractions $<2\ \text{mm}$ from the Ck horizon. X-ray diffraction shows that these are composed of calcite and a low proportion of quartz. Electron microscopy does not show palygorskite fibres on these nodules (Fig. 6). Pieces of yellowish marly limestone, composed of calcite, quartz and clay minerals, have also been collected from these fractions. The electron microscopy study shows palygorskite fibres and small, equidimensional, stubby particles that resemble cristobalite crystals. On the basis of the above association, it appears that palygorskite nucleates preferentially on inorganic crystalline substrates, such as sand and silt-sized calcite or gypsum crystals, although coatings of quartz, feldspar and hornblende have also been reported (Singer 1984). In these soils, palygorskite coating quartz has been also found, although sporadically (Fig. 7). Chemical analysis by energy-dispersive X-rays shows that the substrate is constituted only of silicon.

Discussion

The characteristics of the Ap and AB horizon in these soils are different from those of the other horizons (Table 1). Gravels are present, showing the influence of fluvial processes. The Ck horizon appears as a discontinuity throughout the profile; and is marked by the presence of both secondary calcite, in the form of nodules, and palygorskite. It seems that conditions leading to calcite nodule development are also favourable for the formation of palygorskite *in situ*. Millot *et al.* (1969), Lamouroux *et al.* (1973) and Singer and Norrish (1974) described soils with palygorskite below a calcareous crust horizon, in which the solum above the crust could be at an advanced stage of weathering. These soils have a lower proportion of CaCO_3 in the upper horizon than in the lower horizon, showing a downward movement, with the CaCO_3 deposited at the bottom of the profile. In this study there is a clear relationship between the occurrence of palygorskite and the development of the Ck horizon, suggesting that the environments of the secondary carbonate formations are favourable for palygorskite formation. The fact that palygorskite occurs at the textural boundary has been previously reported (Singer and Norrish 1974; Yaalon and Wieder 1976; Schwaighofer 1980). Palygorskite has not been detected in the upper horizons (Ap, AB and Bk). Kaolinite present in these soils is incompatible with palygorskite and is considered to be detrimental when present in such an assemblage.

The proportion of amorphous silica in Ck horizons is high (7·8% SiO₂ in the <2 mm fraction and 10·03% in the clay fraction). This high proportion is consistent with the presence of cristobalite detected by X-ray diffraction. The concentration is also high in the clay fraction, and it is possible that it exists as gel. Soluble aluminium (Jackson 1969) is also present (0·18% in the <2 mm fraction and 1·06% in the clay fraction).

The presence of cristobalite in sediments has been widely reported. This mineral can be of volcanic or pedogenic origin (Wilding *et al.* 1977). In these soils, it has formed under lacustrine conditions or during sedimentation; the latter is more probable according to its morphological characteristic. Its presence is very important, as it is responsible for the silica-rich environment. The presence of salts also has an important influence on palygorskite formation. These soils are situated in areas with medium rainfall (460 mm), and are only slightly saline (Table 3). The EC is 0·48 mS cm⁻¹; Cl⁻ and SO₄²⁻ are the principal anions, and Ca²⁺, Mg²⁺ and Na⁺ are the principal cations (Table 4).

The formation of palygorskite at textural discontinuities is typical in such soils (Singer 1984). The mineralogical composition suggests the alteration of smectite to palygorskite, as has been proposed by various studies (Yaalon and Wieder 1976; Abtahi 1977; Elprince *et al.* 1979; Martin de Vidales *et al.* 1987). An inverse palygorskite to smectite transformation has also been suggested (Bigham *et al.* 1980; Lee *et al.* 1983).

Weaver and Beck (1977) and Elprince *et al.* (1979) suggested that palygorskite stability is favoured over that of smectite by increases in the activities of either Mg, Si or pH. Thus, when palygorskite is being formed, smectite is dissolving, and vice versa.

All these data, together with palygorskite enrichment in the finest clay fraction and the presence of Mg²⁺ ions, suggest the possibility of authigenic palygorskite formation from smectite, but also suggest that palygorskite is dissolving while smectite is being formed.

Singer and Norrish (1974) have shown that at the concentration of silica normally found in soil solution, palygorskite would not be stable at pH values below 7·7 at high magnesium concentration, nor below pH 9 at lower magnesium levels. The pH of these soils is 7·6 and the magnesium in solution available for the formation of the mineral is very low, so the alteration of palygorskite to smectite is possible.

Under the present conditions of the soil, it is possible that this palygorskite is being transformed into smectite, and this could give rise either to the appearance of a small proportion of palygorskite in some Ck horizons, or to its absence.

The sporadic nucleation of large fibres of palygorskite on silica crystals suggests that the latter mineral could provide the necessary silicon for palygorskite formation, as has been indicated by Singer (1984).

Summary

Palygorskite present in the soils studied in this paper is associated with soil formation with textural discontinuities. Under the present conditions of these soils (pH, magnesium and silicon concentration and soluble salts), the alteration of palygorskite to smectite is suggested.

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