

Structure, properties and genesis of Moroccan palygorskite

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ABSTRACT

The studied palygorskite clay mineral has been collected from several localities of Western High Atlas Tertiary series. Samples characterization has been accomplished by means of X-ray diffraction (XRD), Differential Thermal Analysis (DTA), Scanning and Transmission Electron Microscopy (SEM-TEM) and by Energy dispersive X-ray analysis (EDX). Three types of palygorskite were differentiated, based on the morphology and crystallites. Most of these palygorskite deposits are originally formed in shallow seas and lakes as chemical sediments or by the reconstitution of smectite clays. Structure, mineralogical and chemical purity of these clays are similar than that of the Spanish fibrous clays used in pharmaceutical applications.

Key words: Palygorskite, structure, genesis, tertiary, Western High Atlas, Morocco.

INTRODUCTION

In the Marrakech High Atlas, clay materials represent an important economically source for the region. Eocene clay materials are well known and have been used since ancient times for cottage industry. The first mineralogical study of the Eocene clays was carried out at the Moroccan phosphate basin in the Meseta (North of Marrakech City) by^{1,2}. A detail study of clay assemblages of the Upper Cretaceous to Eocene succession of the western High Atlas was made by³⁻⁵. These authors show that Maastrichtian to Eocene sediments are particularly rich in palygorskite.

Most palygorskite deposits are originally formed in shallow seas and lakes as chemical sediments or by the reconstitution of smectite clays, in open oceans by the hydrothermal alteration of volcanic materials and in calcareous soils by direct crystallization. Natural occurrence of palygorskite

in sediments and soils of arid regions have been widely reported; Tertiary sediments appear to be the main host of palygorskite in the world⁶⁻⁷. Inasmuch as palygorskite had been found in diverse genetic environments, namely marine⁸ bay, lagoon, lake⁹, or soil environments, its mode of formation is not completely understood. Studying palygorskite-rich sediments is therefore helpful to understand the environmental conditions of formation of these fibrous clay minerals in soils and sediments.

The palygorskite clay mineral is an important phyllosilicate with micro-fibrous morphology in industrial applications due to its unique physical and chemical properties¹⁰⁻¹³. It is extensively used in the formulation of various pharmaceutical, cosmetic and other industrial products.

The work reported here, is based on 1) the establishment of the genesis of the palygorskite

in these sediments and 2) the valorization of Western High Atlas (Morocco) palygorskite, where it currently constitutes more than 90% of the clay fraction of some localities.

MATERIAL AND METHODS

About sixty samples consisting of clays, marls and limestones have been investigated by X-ray diffraction on oriented pastes of the less than 2 micrometers fraction of decarbonated sediments. Deflocculation of clays was done by successive washing with demineralised water after removing carbonates from the crushed rock with 0.2 N HCL. The size-fraction <2 mm, was separated by sedimentation according to the procedures described by¹⁶. The XRD analysis was performed using a Philips PW 1730 diffractometer with Cu-Ka radiation and Ni filter. All samples were analysed after air-drying, ethylene glycol solvation and after heating at 490°C for 2 hours. The identification of clay minerals was made according to the position of the basal reflections on the three X-ray patterns¹⁷⁻¹⁸. Semi-quantitative estimations were based on intensity ratios of the 001 reflection of the respective clay species. Transmission and scanning electron microscopic (TEM and SEM) observations have been performed on selected samples, according to the main clay mineralogical assemblages identified by X-ray diffraction. Differential thermogravimetric analyses (DTA) were used to study the weight loss due to dehydration and dehydroxylation. XRF analysis was also performed to study the chemical compositions.

Geological setting

Some detailed and well-documented investigations have already been performed on the clay mineralogy of Late Cretaceous to Eocene sediments from Western High Atlas³⁻⁵⁻¹⁴. We followed the methodological approach implemented by these previous workers to investigate the Eocene series. The Uppermost Cretaceous-Eocene sediments of the Marrakech High Atlas consist chiefly of alternations of marl, dolostone, limestone, gypsum and phosphatic bed. Sedimentary facies and clay assemblages evolution of this series is studied on several sections disposed Eastern to Western part of Marrakech High Atlas (Fig. 1). At the Asni region,

they constitute thick accumulations exceeding 400 meters.

On the North side of the Marrakech High Atlas mountains, the uppermost Cretaceous-Palaeogene series are organised in two sedimentary systems which are separated by a regional-scale discontinuity. The lower sedimentary system with a variable thickness, which is probably of Maastrichtian age¹⁴, comprise elementary sequences composed by alternations of gypsum, occurring as bands and veins, and banks of bioclastic carbonates with marine fauna which became increasingly diversified upwards. Above this, gypsum tends to disappear and the series is composed mainly by bioclastic calcareous and silty sandstones with minor content of phosphate. At the western part of the basin, this unit may be reduced or totally absent. The upper sedimentary system is of Upper Palaeocene to Lutetian age¹⁴. It is composed by two members: (1) lower member; made up of yellow heterogeneous marls and irregular deposits completely absent on the west side. Above, dolomitic bars with marine fauna are present with marl intercalation, followed by phosphate deposits with marl intercalation and thin microcrystalline bioclastic limestones banks, which are hard, partly recrystallized and dolomitized. Both the carbonate and mudrock show mottled appearance; they contain a rich assemblage of planktonic and benthonic foraminifers, together with pelecypods, echinoids, and ostracods. These rocks also contain gypsum and quartz; (2) upper member; made up of a thick series of marls intercalated by thin dolomitic or calcarenite bars with marine fauna,

Table 1: Average chemical composition of palygorskites

Chemical elements	%
Si	18.52 %
Al	3.50 %
Fe	1.79 %
Na	0.11 %
Ca	16.34 %
Mg	12.04 %
K	1.07 %

especially planktonic foraminifera. This series is diversified upward suggesting a deepening trend¹⁴⁻¹⁵. The marls are laminated and consist dominantly of clay and dolomite grains, intercalated by a 5-10 cm thick grey cherty bands consisting of globular bodies.

Clay Mineral Distribution

The clay minerals commonly recognized in the fraction <2 mm of uppermost Cretaceous-Eocene series from the studied sections on the Marrakech High Atlas region comprise illite, smectite, palygorskite, sepiolite and irregular mixed

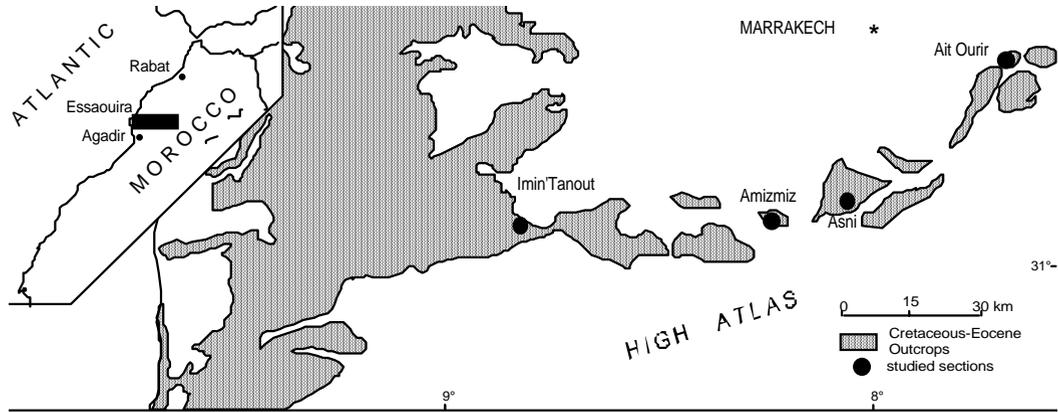


Fig. 1: Location map of the studied region

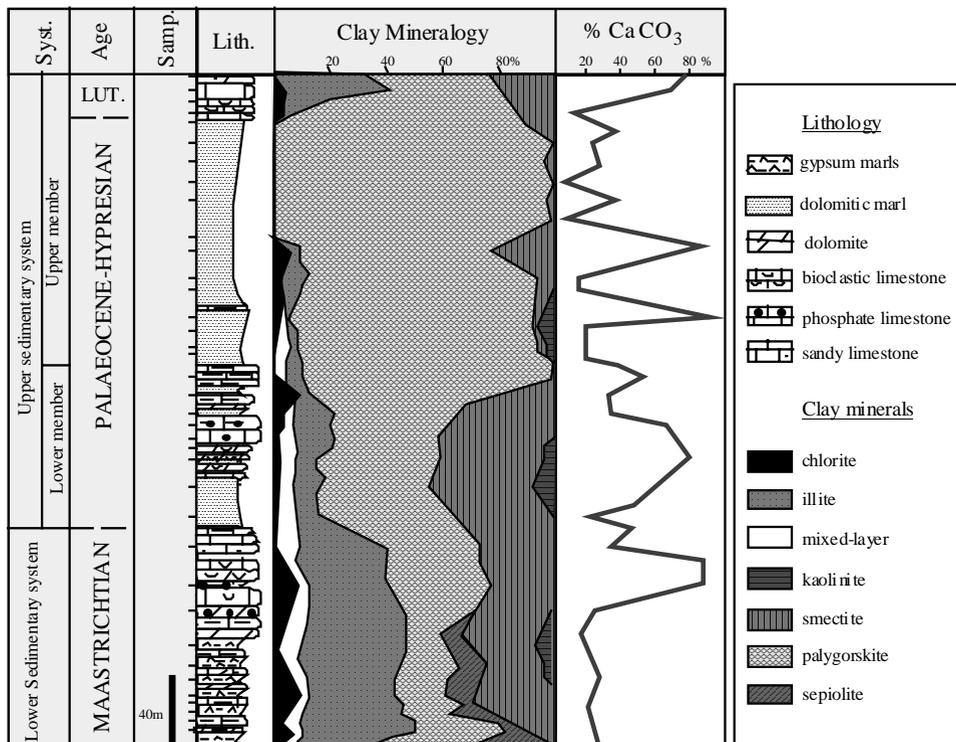


Fig. 2: Clay mineralogy evolution of Asni section

layer. Kaolinite and swelling chlorite occur very locally. Non-clay minerals in the <2mm fraction include common quartz, feldspars and gypsum and occasional goethite or opal. The Asni section displays very clear vertical changes of the clay composition in sedimentary formations (Fig. 2).

In the lower member of upper sedimentary system, palygorskite and smectite are the more abundant and ubiquitous minerals. Palygorskite constitute usually 30 to 60 % of the clay species, and smectite 30 to 45 %. In the upper member, palygorskite content increases (60 to 80 %) when smectite decreases. At the top of dolomitic marls, it reaches unusually high values, where it represents 90 to 100 % of the clay fraction of some samples. In the other sections the composition of clay associations displays the same significant trend, with minor differences. The relative abundance of palygorskite tends to increase upwards in the upper most part of the sections; the amounts of illite and smectite tend to decrease upward. Sepiolite is more abundant in the clayey-gypsum facies of the lower sedimentary system.

Chemical and Mineralogical Results

X-ray diffraction patterns of various samples of palygorskite show a prominent reflection peak from 110 at 10.517 Å and a reflection peak from 220 at 6.45 Å (Fig. 3).

The average chemical compositions of samples determined by XRF analysis is indicated in the table 1.

According to the TEM and SEM analysis, the results obtained show that three types of palygorskite are differentiated, based on the morphology and crystallites.

The type I displays bundle of long fibres under the electron microscope and is associated with carbonate and gypsum facies (Fig. 4, A and B). This type of palygorskites is characterized by high crystalline structure, high specific surface area and excellent sorptive capacity

The type II constitutes thick bundles of short, unbroken and unscattered, flexuous fibres, and appears as overgrowths on pre-existing, possibly smectitic minerals (Fig. 4, C and D).

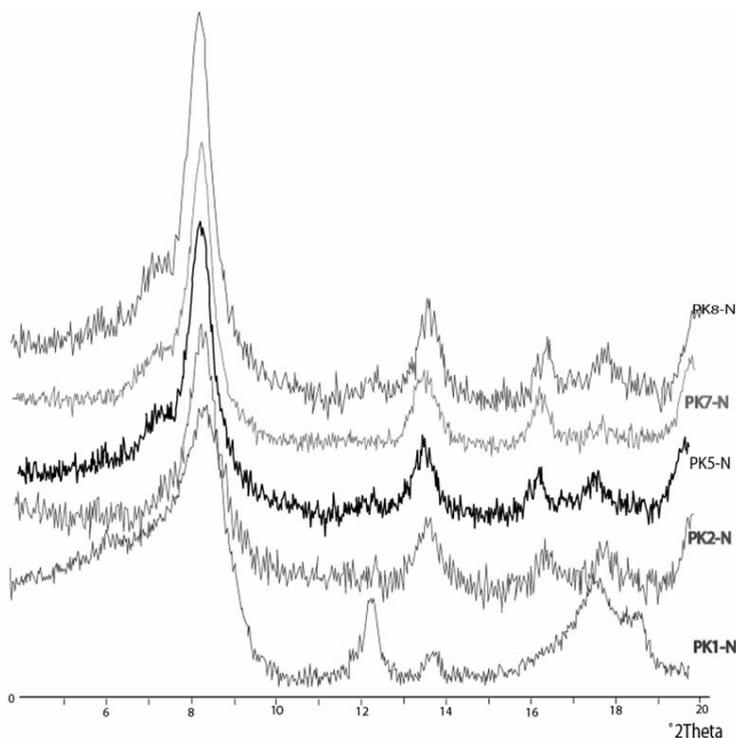


Fig. 3: X-ray diffractograms of Palygorskites of the studied samples

The type III was found in detrital sediments as bundles of shorter and broken fibres (Fig. 4, E and F).

According to the TGA and DTA results, four obvious weight-loss steps are observed (Fig. 5). Most absorption peaks corresponding to the loss of absorption water and zeolitic water are located

at 100 °C to 120 °C. The second weight loss is observed at the peak of 250 °C; it is assigned to the dehydration of the coordinated water binding to M3 sites and the tunnels folded. The third peak related to temperature of 450 °C (type III) and 500 °C (type I and II) can be attributed to the crack of hydration of the residual coordinated water, or to the presence of overlapped sub-peaks due to the

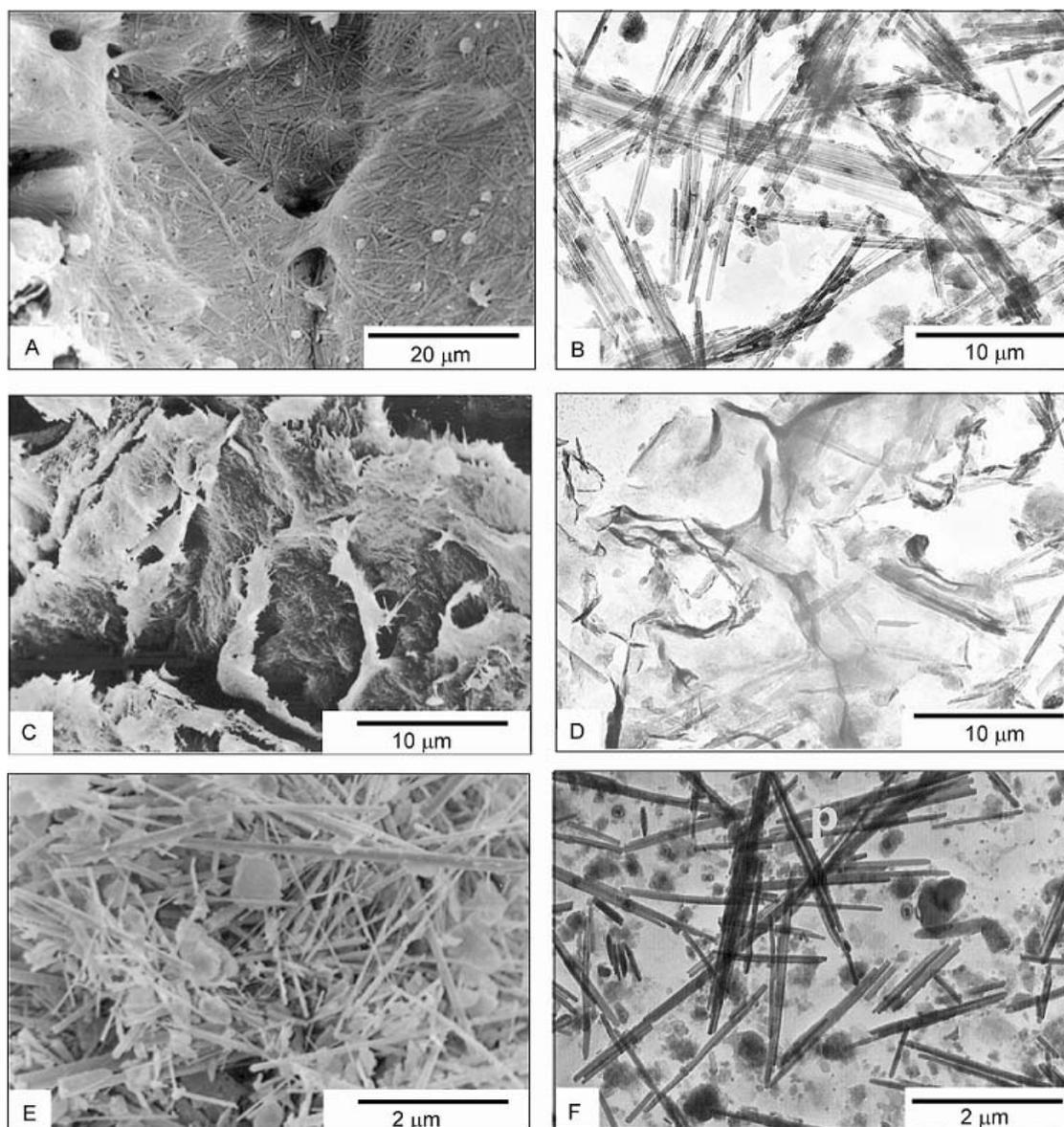


Fig. 4: Scanning and Transmission electron micrographs of different types of palygorskite (type I : A, B ; type II: C, D and type III: E, F)

dehydroxylation corresponding to the different occupations of octahedral sites. The fourth peak is located between 800 °C and 850 °C for the type III, and at 900 °C for the type I and II. It is an exothermic peak which can be or not preceded by an endothermic one.

Palygorskite genesis

Textural evidence shows that the type I and type II palygorskite are authigenic and formed after than the dolomitisation of the Eocene succession of the Marrakech High Atlas. Fine, delicate fibers and fibrous mats of palygorskite in these rocks preclude a detrital origin.

The SEM study shows type I palygorskite as fibrous mats and bundles forming the laminae in the marls and as interwoven fibrous mats and fibres occurring as coatings and pore-filling and pore-bridging cements in the dolomitic marls (Fig. 4, A and B). These textural features suggest direct chemical precipitation from Mg-rich solutions. The conditions necessary for palygorskite genesis have been specified as high Mg and Si activity with some Al and a pH of about 8 [6-19]. Singer²⁰ pointed out that if palygorskite coexists with dolomite, the concentration of Mg in solution has been found to be adequate for palygorskite formation. Therefore,

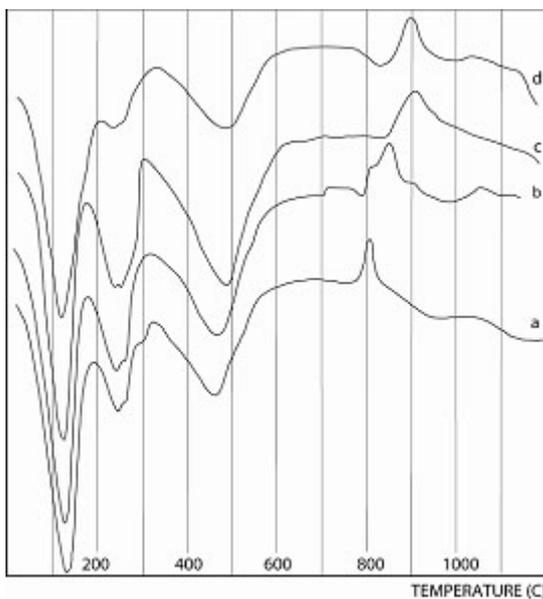


Fig. 5: ATD curves of type III (a and b) and type I-II (c and d) palygorskites

Mg concentrations of the mixed fresh-marine waters were sufficient to cause dolomitisation and the subsequent precipitation of palygorskite. The source of Mg is believed to have been sea water. Chert is common in thin layers and solution cavity fillings particularly in the upper member of the upper sedimentary system, suggesting the availability of an ample supply of silica for the formation of palygorskite. The silica and alumina may have been released from detrital quartz and silicates under high pH conditions.

The type II palygorskite textures suggest a transformation from smectite minerals. The mode of formation of palygorskite through transformation from smectite has been considered unlikely because of significant differences in the structures of the two minerals [20-21]. However, textural evidence found in the present study (Fig. 4, C and D) suggests clearly the formation of palygorskite by solid-solid transformation of smectite. The inverse relationship between the relative abundance of the two minerals in the section (Fig. 2), suggest the alteration of smectite to palygorskite. This mode of formation of palygorskite is described by [6-22-23].

The type III is identified mainly in the lower part of the section (Fig. 4, E and F); in the lower sedimentary system and in the lower member of upper sedimentary system (Fig. 2). In these levels, the palygorskite content doesn't exceed 40 % of the clay fraction. This type of palygorskite was found in detrital sediments as bundles of shorter and broken fibres. These palygorskite suggest a detrital origin and probably result from reworking authigenic palygorskite.

The widespread occurrence of palygorskite in the upper member of upper sedimentary system suggests that the formation of palygorskite was not dependent on salinity and that it formed continuously at variable rates. The presence in some samples of lower sedimentary system (Maastrichtian) of gypsum locally coated by palygorskite, suggests that palygorskite also precipitated from hypersaline solutions during dry intervals. The rise in the relative and absolute abundances of palygorskite in the upper member is probably due to a rise of sea level (local transgression described by¹⁴⁻¹⁵).

Occurrences of palygorskite in various restricted and semi-restricted basins have been documented by previous workers [6-8-24]. These studies stressed the importance of basin morphology and, to a lesser extent, climate for the formation of this mineral. The presences of palygorskite, along with smectite, suggest a hot (arid to semiarid) climate with some rainy intervals. The occurrence of detrital illite and chlorite suggest a reduced intensity of chemical weathering under dry climates²⁴. Thus, during the deposition of the Palaeocene-Eocene succession in the Marrakech High Atlas, the climate was probably arid to semiarid with some humid intervals. The alternating presence of minor amounts of chlorite and kaolinite in the succession was probably due to the dry and more humid intervals, respectively.

CONCLUSION

The widespread occurrence of palygorskite in the Tertiary sedimentary series of the Marrakech High Atlas suggest its formation in restricted and semi-restricted basins, under hot (arid

to semiarid) climate with some rainy intervals. This study stressed the importance of basin morphology and, to a lesser extent; climate for the formation of this mineral.

The comparison of these results with those of Spanish fibrous clays (palygorskite) used in pharmaceutical applications, shows that structure, mineralogical and chemical purity of the type I clay minerals are similar than that of the Spanish fibrous clays. This type of fibrous clay is the most abundant one in the Tertiary sedimentary series of the Western High Atlas area.

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