



Mineralogical and physico-chemical characterization of Mbodiene palygorskite for pharmaceutical applications



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ABSTRACT

This contribution provides a wide morphological, mineralogical, chemical and physical characterization of Mbodiene palygorskite (Senegal), to serve as a basis for the formulation of anti-diarrheal and cosmetic products. Data are compared with other palygorskite deposits, either in Senegal or on other continents.

Qualitative total rock XRD, semi-quantitative XRD of the clay fraction and quantitative X-Ray fluorescence (XRF) show the presence of 72%wt palygorskite ($\pm 2\%$ wt), 13%wt montmorillonite ($\pm 2\%$ wt), 8%wt dolomite ($\pm 2\%$ wt), 5%wt quartz SiO₂ ($\pm 2\%$ wt) and 2%wt inter-stratified illite/smectite ($\pm 2\%$ wt). Coupled SEM + EDX and TEM + EDX confirm the presence of fibrous palygorskite, with greater amounts of Mg than Al, and Fe substitution to Mg and Al, interspersed with dolomite cubes CaMg(CO₃)₂. The presence of carbonates in Mbodiene palygorskite may limit its use in the Pharmacopoeia, and make its purification necessary.

A specific signature of Mbodiene palygorskite, relevant to the palygorskite family, is deduced from both FTIR and TGA analysis. In terms of physico-chemical characterization, Mbodiene palygorskite has usual values when compared to the literature (for its specific surface area, specific gravity, compressibility and Hausner indexes, CEC, loss on ignition, etc.). After grinding (down to a peak grain size of 500 nm), Mbodiene palygorskite is considered a normal clay, extremely highly plastic, with hard consistency owing to the values of its Atterberg plasticity and liquidity limits, with good flowability owing to its compressibility and Hausner indexes. Its physical characteristics are suitable for manufacturing pastes and colloidal suspensions.

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1. Introduction

1.1. Scientific context

Palygorskites and sepiolites are fibrous clays of the inosilicate family, similar in crystal arrangement to amphiboles, with a ribbon-like structure. At the scale of the elementary layers, sepiolites are trioctahedral clays, whereas palygorskites are dioctahedral (Meunier, 2005; Murray et al., 2006) (Fig. 1). Palygorskites are also more common than sepiolites. They are double aluminium and

magnesium silicates of general formula ((Mg, Al)₂ Si₄ O₁₀ (OH).4H₂O) (Caillere and Henin 1961a,b; Caillère et al., 1982; Moore and Reynolds 1997; Rautureau et al., 2004; Post and Heaney, 2008), with possible substitutions of Fe to Mg and Al. (see Fig. 11)

Their specificity is their tridimensional arrangement at the nanometric scale. The clay particles (or rather fibers) are in the form of 2D ribbons or 3D hollow tubes, also called canals, channels, or canalicules. The latter are built by the connection of 2/1 tetrahedral-octahedral-tetrahedral (TOT) layers by an apical oxygen atom, contrarily to usual lamellar phyllosilicates (Fig. 1a and b). Owing to this oxygen atom connection, tetrahedral silicate layers (T

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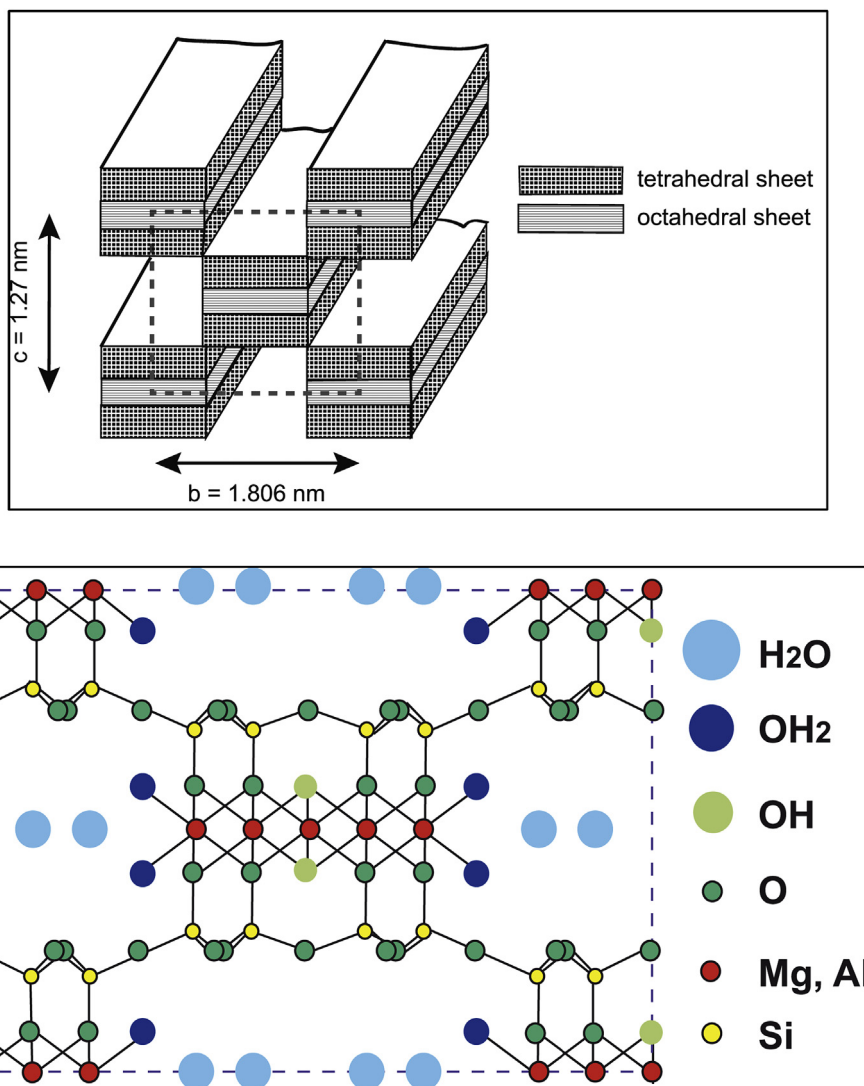


Fig. 1. 2/1 tetrahedral-octahedral-tetrahedral (TOT) layer arrangement of palygorskite clay at the scale of the particle (or fiber), (a): Bradley's model, after (Poppe et al., 2001) and (b): atom arrangement in a [001] projection plane, after (Bailey, 1980; Poppe et al., 2001) (H_2O is zeolitic water; OH_2 is bound water). The chain-like structure of palygorskite is evidenced by these representations.

are continuous, whereas the octahedral magnesium or aluminium layers (O) are of a discontinuous chain-like nature, allowing structural ribbon- and tube-like morphologies.

The palygorskite fiber contains three types of water (Fig. 1b). Bound (or hydroxylic, constitution) water is coordinated to the octahedral cations through its OH group by the strongest covalent-type bonding; strong hydrogen bonds link water molecules (of the so-called crystallisation or zeolitic type) to the octahedral cations; finally, weaker Van der Waals bonds attach water molecules to neighbouring ones located at the clay surface. Zeolitic water (on the order of 12%) is reputed fully removed by heating at 120°C .

The elongated morphology and the presence of the channels are the most important physical attributes of palygorskites. Their 3D arrangement provides them with a high specific surface area and a high sorptive capacity, while their elongated shape prevents particle flocculation in liquid solutions (Murray et al., 2006). The length of palygorskite fibers varies greatly, from below $1 \mu\text{m}$ to almost $20 \mu\text{m}$, with an average between 1 and $2 \mu\text{m}$, and a diameter of $0.1\text{--}0.5 \mu\text{m}$ (Singer, 2002). Palygorskite fibers are often arranged in bundles or sheaths.

1.2. Industrial context

Over geological timescales, most major deposits for palygorskites have been formed in shallow seas and lakes (as chemical sediments or by the reconstitution of smectites), in open oceans (by the hydrothermal alteration of volcanic matter), and in calcareous soils (by direct crystallization) (Callen, 1984). The magnesium necessary for their formation is generally brought by the reaction of detrital materials with brines or magnesium salts resulting from sea water evaporation (Patterson 1974; Murray et al., 2006; Rautureau et al., 2004). Whenever the amount of Si and Al is insufficient, dolomite can form instead of palygorskite. The name 'palygorskite' was given after the place in the Ural Mountains (Palygorskaya on the Popovka River, Permskaya Oblast, Russia) where it was discovered in 1862, while 'attapulgitite' is the particular name given in 1935 to the palygorskite originating from the Attapulgitus deposit (Georgia, South East USA). They have also been named hormites, but the International Nomenclature Committee of the AIPEA (Association Internationale Pour l'Etude des Argiles, i.e. International Association for the Study of Clays) and the

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