

Tracing the depositional microenvironment and related genetic mechanisms of Fe-rich palygorskite and Mg-Fe-smectite in the Velanida clay deposit, western Macedonia, Greece

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The Velanida clay deposit composed of Fe-rich palygorskite and Mg-Fe-smectite rich clays, is situated within the so called “Ventzia” basin, located approximately 7 km southwest of the town of Eani in Kozani prefecture, Greece. This clay deposit lays unconformably on ultramafic rocks of the Vourinos ophiolitic complex and Mesozoic limestones of the Pelagonic Unit. The clay sediments were deposited in a fluvial-lacustrine rift basin formed during the Upper Pliocene – Lower Pleistocene period and grade east into the upper layers of the “Servia” Neogene basin that consists primarily of magnesium rich carbonates, dolomitic marlstone and sandstone (Stamatakis, 1995). According to a generic model by Kastiritis *et al.*, (2003), the initial sediment supply into the basin was mainly fine-grained serpentine sands and Mg-Fe-smectite clays that eroded from the saprolite bodies formed on the Vourinos ophiolite complex and the smectite-bearing sands of the Mesohellenic trench. During the closure of the basin sediment supply shifted, producing a high energy detrital deposit composed of carbonates mostly derived from the Triassic crystalline limestones located to the north of the deposit.

Fe-rich palygorskite and Mg-Fe-smectite rich clays from the deposit were characterized by combining geological (stratigraphy), mineralogical, geochemical, sedimentological and micropaleontological data to better understand the depositional microenvironment and their related genetic mechanisms. Methods utilized for the current study included X-ray diffraction (XRD), scanning electron microscopy (SEM) coupled by energy dispersion spectrometry (EDS), chemical analysis and micropaleontological investigation.

Stratigraphy data based on the evaluation of over 100 exploratory boreholes reveal the presence of three distinct Mg-rich clay layers, alternating with gravelly clays, with a total thickness of approximately 50 - 70 m that dip gently to the southeast at angles ranging from 5° to 10°. The clay-rich layers include from the bottom of the sequence: 1) a green/brownish Mg-Fe smectite rich layer (A1) with a total thickness of 30 to 40 m, 2) a greyish palygorskite-rich layer (A2) with a total thickness of approximately 15 m, and 3) a greyish/greenish white or brownish purple mixed palygorskite-smectite layer (A3) with a total thickness of nearly 20 m. Carbonate concretions composed of calcite – dolomite mixtures are observed at the base of the A2 layer, mainly in globular form less than 1 cm wide. The overburden material consists of overlying Pleistocene carbonate sediments whereas the interburden material consists of intercalating clastic sediments such as micro-conglomerates and loose sand of serpentine origin and sandy clays of serpentine and smectite origin.

Mineralogical analysis by XRD was conducted on representative clay samples collected from the exploratory boreholes. The main mineral phases identified are palygorskite or /and Mg-smectite while serpentine, dolomite, calcite and quartz are accessory phases. Mineralogical data in combination with sedimentological and stratigraphy data determine a general, lateral grading in the Velanida deposit that portrays palygorskite rich clays in the center grading to mixed palygorskite-smectite clays and to smectite rich clays that alternate with sandy clays and serpentine sands towards the outer rim of the deposit. Coarser detrital sediments of serpentine sand and gravel, and smectite clayey sands were deposited at the outward part of the deposit.

The SEM study revealed the presence of several forms of palygorskite lath assemblages regarding the length or the orientation of the fibers, the density and the intergrowth between them and the void spaces in skeletal textures of laths. Moreover, palygorskite laths have been observed to develop on the surface of Fe-Mg-smectite flakes or to intergrow with rhombohedral dolomite crystals. All the above are indicative of the deposition micro-environment conditions related to palygorskite formation mechanisms (Garcia-Romero *et al.*, 2013).

Chemical analysis was performed on about 50 representative clay samples collected from exploratory boreholes for main oxides and trace elements. Geochemical analysis of chemical data was completed by plotting the relative concentrations of major oxides on ternary diagrams as well as by statistical analysis for the preliminary evaluation of possible geochemical reactions during deposition/diagenesis of the clays. Concerning major oxides, Velanida palygorskite clays exhibit low Al₂O₃ (4.3 % on average) and high MgO (12.7 % on average) and Fe₂O₃ content compared to typical palygorskite clays from Attapulgis clay deposits of Georgia and Florida, USA. Although Fe-rich palygorskites are scarce (Suarez *et al.*, 2011), the Fe₂O₃ content of palygorskite from the Velanida clay deposit is high ranging from 11.2 to 14.6 %.

Micro-paleontological data were co-evaluated, concerning Mg-clays genesis, to explore a probable link to a climatic change from a humid subtropical climate to a more arid or semi-arid climate of the Upper Pliocene and to provide insights into the general paleo-environmental conditions and the depositional environment of the clay deposit. Representative samples of palygorskite and smectite rich clays were pretreated following standard palynological procedures to prepare them for palynological-palynofacies analysis. The protocol followed included reaction of the sediment with strong acids in repeated steps, to remove the inorganic clasts, acetolysis and finally sieving the residue to collect the less than 7 µm fraction. Recovered palynomorphs include pollen, fungal remains, algal spores, as well as microscopic charcoal particles.

Pinus, *Cedrus*, *Picea* and *Tsuga* are some of the tree pollen recovered, while herb vegetation includes Ericaceae and Poaceae.

According to the findings of the present study combined with an extensive review of the international literature regarding palygorskite formation, three distinct genetic processes are considered with respect to the Velanida palygorskite mineral assemblage: 1) diagenetic formation through the full expense of Mg-smectite clays as documented in the Carrion lacustrine basin of central Spain (Sanchez *et al.*, 1995), in the calcretes of the Duero and Tajo basins from central Spain (Rodas *et al.*, 1994), in a Mg-rich environment of the Neogene Madrid basin from Spain (Pozo *et al.*, 2016) and in the Attapulugus region from southern Georgia-northern Florida, USA (Moll, 2001), 2) pedogenesis related processes such as incomplete dissolution of Mg-smectite and precipitation as identified in soils of Maharashtra, India (Hillier *et al.*, 2008) and in the Chinese Loess Plateau of northwest China (Xie *et al.*, 2013) and 3) chemical precipitation from solutions rich in Mg, Si and Al as revealed in the Tertiary lacustrine formation of Jbel Rhassoul, Morocco (Chahi *et al.*, 1993), in the Cretaceous paleosols of the Bauru Basin, Brazil (Silva *et al.*, 2018) and in the fluvial-lacustrine Serinhisar-Acıpayam basin of western Anatolia, Denizli, Turkey (Akbulut *et al.*, 2003). Combined action of the above processes cannot be excluded, similarly to palygorskite formation in SW Eskisehir, Turkey where chemical precipitation in an alkaline lake environment rich in Al and Fe under semiarid or arid conditions and transformation from saponite during diagenesis, have been suggested as the main processes, (Yeniyol, 2012). In our study the main mechanisms of Velanida palygorskite formation were probably both, complete diagenetic transformation of Mg-smectite, more evident in the clay layer A2, and partial dissolution of Mg-smectite followed by precipitation of palygorskite as manifested in the mixed palygorskite-smectite clays of layer A3. Chemical precipitation from saturated solutions rich in Mg, Si and Al was much more limited and local.

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