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The palygorskite and Mg-Fe-smectite clay deposits of the Ventzia basin, western Macedonia, Greece

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ABSTRACT: Sedimentary ore deposits of palygorskite and Mg-Fe smectite clays were discovered recently by I. D. Kastritis of Geohellas S.A. in the "Ventzia" continental basin, east of Grevena in western Macedonia, Greece. The deposits are Late Pliocene to Early Pleistocene in age and consist of several series of palygorskite and smectite beds that grade into mixtures of palygorskite with smectite. The large size of these deposits and their occurrence outside of the world's known attapulgite districts is of great geological as well as economic significance. At present, detailed geological work has been completed on two of the Ventzia basin deposits: the Pefkaki deposit and the Pilori deposit. These two deposits contain total proven reserves of 6 m.t. (million tons) of palygorskite clay (60-95% palygorskite), 4 m.t. of smectite clay, and 3 m.t. of mixed palygorskite/smectite clay. Probable reserves for the entire basin exceed 50 m.t. of palygorskite and smectite clays. The geological data indicate that the smectite clays formed by transformation of pre-existing smectitic material that was transported into the basin from two different sources: the altered ultramafic rocks of the Vourinos complex and the smectite-bearing sands of the Mesohellenic trench. The palygorskite clays appear to have formed diagenetically by in-situ reaction of smectite with silica rich solutions.

1 INTRODUCTION

Industrial-scale palygorskite deposits are confined to relatively few locations worldwide, with the most well known deposits occurring in the Georgia-Florida attapulgite district of the USA. The present study concerns the recent discovery of extensive palygorskite and palygorskite/smectite deposits in western Macedonia, Greece. In the course of mine development activity, Geohellas S.A. has completed research on two of the clay deposits in this area. The purpose of this paper is to present the geology and economic geology of these clays and to communicate some initial thoughts on their genesis.

2 GEOLOGICAL SETTING

The Ventzia basin, as we define it here, is found northeast of the city of Grevena. It has a maximum width of 6 km, a length of 22 km, and area of ~70 km^2 (Fig. 1). This basin represents a small section of a much larger continental basin that developed in western Macedonia during the Late Pliocene/Early Pleistocene.

The basement of the Ventzia basin consists mainly of ultramafics of the Vourinos ophiolite complex and molassic sediments of the Mesohellenic trench. Smectite-bearing saprolite was detected on the ophiolitic basement while smectitic/serpentinitic sands and sandstones were detected within the molasse of the Mesohellenic trench. No palygorskite was identified within the rock basement.

The Ventzia basin is highly clastic in nature. The petrography of its coarse sediments is directly related to the rock basement. The sediments lie unconformably on the rock basement and are generally horizontal with a maximum thickness of nearly 200 m.

A representative lithological column of the basin includes four series: a) loose gravel or loosely connected gravel and pebble conglomerates and sands (basal series), b) a lower series of smectite clay and sandy clay with intercalated beds of gravel with a maximum thickness of 150 m, c) an upper series consisting mainly of palygorskite clay beds, 2 to 6 m thick, with a total maximum thickness of 18 m, and d) a ceiling series of beds that consist of loose pebble, gravel, and sand with numerous thin lenses of smectite and palygorskite/smectite mixtures.

Irregular lenses and networks of dolomitic material were observed in many locations mainly within smectite clay. Silicified clay, gravel and dolomitic material were also observed in numerous locations, especially near palygorskite clays.

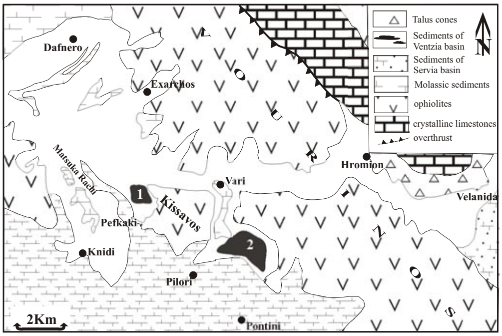

Figure 1. Geological map of the Ventzia basin (geological map of Greece, sheet Knidi, I.G.M.E., 1993). 1: Pefkaki deposit, 2: Pilori deposit.

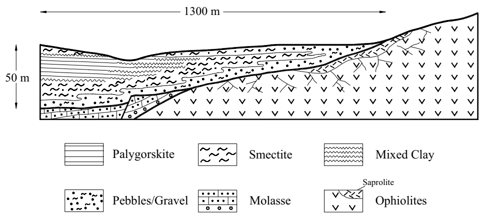

Figure 2. Schematic cross section from Pilori palygorskite and smectite deposits.

3 MINERALOGY-PETROGRAPHY OF THE VENTZIA PALYGORSKITE AND SMECTITE CLAYS

A detailed mineralogical investigation by X-ray diffraction, by differential thermal and thermogravimetric analysis, and by optical and electron microscopy have been performed on bulk samples. The results of these studies reveal that the clay beds of the Ventzia basin consist of palygorskite, smectite, and mixtures of smectite and palygorskite. In addition, mixtures of palygorskite with sepiolite and smectite with sepiolite have been identified in some discrete beds (cm-dm in thickness).

3.1 *Palygorskite clays*

Beds in which palygorskite predominates have a greenish, grey purple or brownish-green color. After drying, the palygorskite turns a light color and/or white. In these beds, palygorskite concentrations range from 60-95% (Fig. 3). A TEM photograph of a representative palygorskite sample from the Pefkaki deposit is given in Figure 4. Quartz, smectite, and platy serpentine (lizardite and/or antigorite) are the most common minor phases. Interestingly, no calcite is observed in the palygorskite clay samples.

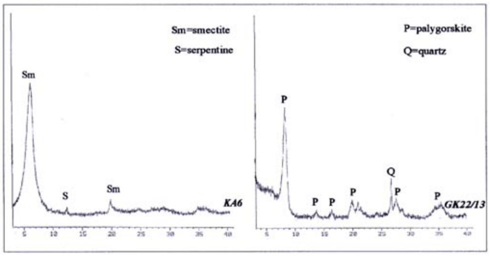

Figure 3. X-ray diffractograms of representative smectite and palygorskite clays from the Ventzia basin (western Macedonia, Greece) over a range of 3° to 40°, using Cu Kα radiation.

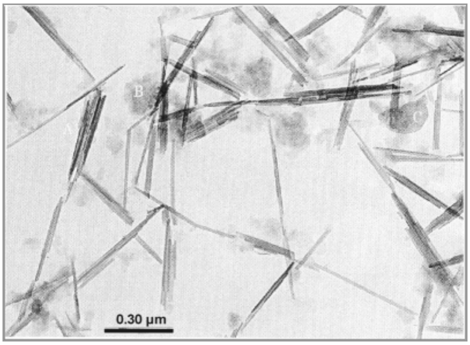

Figure 4. TEM image of palygorskite from the Pefkaki deposit.

3.2 *Smectite clays*

Smectite beds have a greenish, green-yellowish, brownish or red-brownish color and a waxy appearance. Smectite concentrations in these beds range from approximately 60-95% (Fig. 3). In XRD, the smectites display a basal spacing near 15 Å in the air-dried state, which is consistent with the presence of Ca^{2+} and Mg^{2+} as major interlayer ions. The smectites expand completely upon ethylene glycol solvation, and significant mixed layering with other clays appears to be absent. The average position of the d(060) peak occurs near 1.51 Å, suggesting that these smectites are of intermediate trioctahedral/dioctahedral character. Platy serpentine, quartz, plagioclase, palygorskite and dolomite are the most common minor phases.

3.3 *Palygorskite-smectite mixtures*

Beds containing mixtures of palygorskite with smectite clays represent transitional zones within this basin. In the field, these beds display colors ranging from green to purple/grey. They commonly display a waxy appearance when wet, but upon drying attain a low bulk density and adhere to moist surfaces like palygorskite. Quartz, platy serpentine, and occasionally dolomite, occur as additional minor phases.

4 CHEMICAL COMPOSITION OF THE VENTZIA PALYGORSKITE AND SMECTITE CLAYS

Chemical analyses were performed on bulk samples that consisted of 90 to 95 % palygorskite and 90 to 95 % smectite. The palygorskite rich samples yielded 58.5 to 60 % SiO_2, 6.34 to 12.6 % MgO and 6.3 to 8.2 % Fe_2O_3 as total iron. The smectite rich samples yielded 52 to 56.5 % SiO_2, 8.5 to 14 % MgO and 9.5 to 13 % Fe_2O_3 as total iron. The results of the chemical analyses reveal that the palygorskite clays are richer in SiO_2 than the smectite clays, while the smectite clays are richer in Fe_2O_3. Even though MgO appears slightly higher in the smectite clays (Mg-Fe-smectites), we can assume that the MgO content of both clays is similar. On the other hand, the concentration of MgO in the smectitic sands derived from the basement rocks is higher, ranging from 12.4 to 24 %.

Table 1. Chemical analyses of Ventzia palygorskite and smectite.

Sample	Pal GK22/13	Sm KA6
SiO_2	58.70	53.50
TiO_2	0.33	0.20
Al_2O_3	6.47	4.53
Fe_2O_3	8.15	12.70
MnO	0.12	0.03
MgO	12.20	14.0
CaO	0.27	0.83
Na_2O	0.09	0.05
K_2O	0.53	0.02
LOI	11.90	13.18

Oxide compositions and approximate structural formulae for the palygorskite and smectite samples shown in Figure 3 are given in Tables 1 and 2. In calculation of the formulae, iron was assumed to be in the ferric state. The allocation of Mg to exchange sites of the smectite was based on the CEC value determined by methylene blue absorption analysis: 85 meq/100g. As shown in Table 2, the smectite possesses a high proportion of Mg in its exchange sites and has a composite structure of dioctahedral and trioctahedral smectite with a trioctahedral component of 32%. The palygorskite is rich in Mg and Fe and is significantly poorer in Al than palygorskites from Spain (Torres-Ruiz et al., 1994) and the Attapulgus district of Georgia (in Jones and Galan, 1988), indicating that protoliths poor in Al and rich in Mg and Fe were involved in the formation of the Ventzia palygorskite clays. We believe that these protoliths are the Vourinos peridotites that comprise a large part of the Ventzia basement rocks.

Table 2. Structural formulae of Ventzia palygorskite and smectite.

Palygorskite (GK22/13):*
$(Si_{7.72}Al_{0.28})(Al_{0.77}Fe^{3+}_{0.91}Mg_{2.52})_{4.20}Ca_{0.04}Na_{0.02}K_{0.09}O_{20}(OH)_2(OH_2)_4$

Smectite (KA6):
$(Si_{7.74}Al_{0.26})(Al_{0.51}Fe^{3+}_{1.47}Mg_{2.65})_{4.64}Ca_{0.13}Mg_{0.37}Na_{0.01}O_{20}(OH)_4$

*corrected for 3% quartz

5 PHYSICAL PROPERTIES

An extensive investigation conducted by Geohellas S.A. on the physical properties of clays from the Ventzia basin indicates that these clays are capable of serving in a wide variety of sorptive and thixotropic applications. Properties data for palygorskite, smectite, and mixed palygorskite/smectite are given in Table 2. In general, the properties of Ventzia basin clays vary, as expected, with the proportion of palygorskite and smectite in the bulk material. Additionally, however, some synergistic effects are observed in materials in which palygorskite and smectite occur together as natural mixtures. These mixtures, for example, are capable of producing exceptionally high viscosity values.

Table 3. Some properties data for Ventzia palygorskite, smectite, and mixed clay.

Property	Palygorskite (60-95%)	Smectite[(d)] (60-95%)	Mixed Pal/Sm[(d)] (X_{pal} = 0.3-0.5)
Bulk Density, g/cc[(a)]	0.45-0.6[(e)]	0.9-1.0	0.7-0.85
Water Abs., %[(a)]	100-220[(e)]	200-280	140-240
Oil Abs., %[(a)]	90-120[(f)]	40-70	60-80
Dispersion Viscosity, cps[(b)]	3500-4500[(g)]	3000-6000	5000-8000
API Viscosity[(c)]	27-45[(g, h)]	30-55[(i)]	60-80[(i)]

[(a)] 30/60 mesh fraction, [(b)] 7% clay in DW, Brookfield RVT Viscometer with #4 spindle, [(c)] API Spec. 13A, 600 rpm reading, [(d)] Soda-activated, [(e)] Sample dried as 150°C ("RVM grade"), [(f)] Sample calcined at 450°C ("LVM grade"), [(g)] MgO activated, [(h)] in salt water, [(i)] in fresh water.

6 ECONOMIC GEOLOGY

At present, Geohellas SA has examined in detail drill core data from two deposits in the Ventzia basin: the Pefkaki deposit and the Pilori deposit. The Pefkaki deposit is located northeast of the village of Knidi and covers an area of about 0.4 km^2. The maximum thickness of the clay in this deposit is 15 m, while the total thickness of palygorskite beds reaches 10 m. The stripping ratio of the Pefkaki deposit ranges between 0.3 and 3.

The Pilori deposit is located northeast of the village of Pilori and covers an area of about 1 km^2. The maximum thickness of the clay in this deposit is 30 m, while the total thickness of palygorskite beds reaches 18 m. The stripping ratio of the Pilori deposit ranges between 0.2 and 1.5.

Total reserves of these two deposits are 6 m.t. (million tons) of palygorskite clay (60-95% palygorskite), 4 m.t. of smectite clay, and 3 m.t. of mixed palygorskite/smectite clay.

7 DISCUSSION

The Ventzia basin is a continental basin with high clastic sedimentation rates. While this does not preclude direct chemical precipitation of palygorskite and smectite on a small scale, it does not seem likely that direct chemical precipitation could have contributed significantly to the formation of such thick palygorskite and smectite deposits. Rather, there is strong evidence for the formation of these clay deposits by diagenetic processes. In fact, the lateral grading of smectitic sands into smectite clays indicates a progressive transformation of a pre-existing sandy smectitic material to a typical smectite clay. The presence of irregular lenses and networks of dolomitic material within the smectite clays indicates that the above mentioned transformation released MgO. We believe that this pre-existing sandy smectitic material originated from two sources: the Vourinos saprolite and the Mesohellenic molasse.

The lateral grading of smectite clay to smectite-palygorskite mixtures and finally palygorskite, coupled with evidence of silification processes, reveal that palygorskite was formed diagenetically by in-situ reaction of smectite with silica rich solutions. It appears that this reaction was associated with release of Fe_2O_3. These observations are in accordance with the mineralogical and chemical data.

8 CONCLUSIONS

The large size and high quality of the recently discovered palygorskite deposits in western Macedonia, Greece, far from the world's large palygorskite deposits, are of great geological as well as economic significance. The palygorskite and Mg-Fe-smectite deposits of the Ventzia basin appear to have originated by diagenic transformation of pre-existing sandy smectitic material. We believe that this pre-existing smectitic material was derived from the basement rocks.

The results of basin-wide research by Geohellas S.A. to date indicate that the palygorskite accumulations of the Ventzia basin are among the largest in the world. Probable, combined reserves of palygorskite and smectite clays exceed 50 m.t.

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