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ΓΕΩΛΟΓΙΑ.— **Clay mineral abundance of shales and slates from some Greek regions through geologic time,** by *E. Chatzidimitriadis, A. Tsirambides and S. Theodorikas*, διὰ τοῦ Ἀκαδημαϊκοῦ κ. Λουκᾶ Μουσούλου.


ABSTRACT

The clay mineral abundance of shales and slates through geologic time, collected from three island and five mainland outcrops of Greece, is studied in this paper. Their age extends from Silurian to Oligocene. Microscopic examination and XRD analysis revealed the existence of discrete and interstratified clay minerals as are: Illite, chlorite, vermiculite, kaolinite, smectite, mica/smectite, illite/smectite, chlorite/smectite and chlorite/vermiculite. Generally, the older samples are richer in illite and very poor in kaolinite and mixed-layer phases. Most shale samples present Kubler Index values between 2.0 and 3.7 meaning that they have undergone late diagenesis. The rest, with values between 3.7 and 7.2, have undergone middle diagenesis. The slate and greenschist samples present K. I. values close to 2.0.


K e y w o r d s: Shale, slates, greenschists, illite, chlorite, vermiculite, kaolinite, smectite, interstratified minerals, Kubler Index, diagenesis, anchimetamorphism, Greece.

## INTRODUCTION

The adjustment mechanisms of clastic weathering materials, which are settled downwards in a depositional basin, have been well studied recently. These mechanisms involve greatly mineralogical changes which depend on the processes of diagenesis and anchimetamorphism. The boundary between them is based upon mineralogical and textural criteria which do not always coincide.

Ε. ΧΑΤΖΗΔΗΜΗΤΡΙΑΔΗ, Α. ΤΣΙΡΑΜΠΙΔΗ, καὶ Σ. ΘΕΟΔΩΡΙΚΑ, **Ἀφθονία ἀργιλικῶν ὀρυκτῶν σὲ σχιστοπηλοὺς καὶ ἀργιλικοὺς σχιστολίθους ἀπὸ ὁρισμένες περιοχὲς τοῦ Ἑλληνικοῦ χώρου διὰ μέσου τοῦ γεωλογικοῦ χρόνου.**

The modifications that affect the clay minerals usually occur at depths exceeding 2 km. The boundary between diagenesis and anchimetamorphism is based on the sharpness (Weaver, 1960) or width (Kubler 1967) of the 10 Å illite peak. According to Weaver (1984) the boundary between late diagenesis and anchimetamorphism is determined by temperatures $250^0$ to $280^0$ C and values of Kubler Index and Weaver Index 3.0 and 2.3 mm respectively.

The most characteristic diagenetic change in clayey sediments involves the conversion of smectite to illite in the interstratified phase of illite/smectite with increasing burial depth. During burial diagenesis a small amount of chlorite rich in iron may be formed as a by-product of the smectite to illite reaction. Reaction, mechanisms of illitization are considered as solid-state (Bethke & Altanen, 1986) or dissolution-precipitation (Pollastro, 1985). Smectites of various types can form from the alteration of a wide range of minerals and rocks. Montmorillonite is abundant in the semiarid region of the eastern Mediterranean where it is inherited mostly from carbonate rocks.

Micaceous material is dominant in all temperate soils. In shales and other sedimentary rocks the micaceous component consists commonly of muscovite and illite. Muscovite is most abundant in the silt fraction and illite and illite/smectite in the clay fraction. In shales the coarse material is usually the 2M polytype and in the fine illite the 1M-2Md polytypes. Conditions favorable for the formation of pedogenic illite may have been extensive in the Paleozoic. The most likely source material for the formation of pedogenic illite or mica is K-feldspar or plagioclase.

Abundant chlorite is commonly generated during the late stages of diagenesis of shales with the simultaneous formation of slaty cleavage. The mixed-layer phases of chlorite/smectite and chlorite/vermiculite, known with the general term of corrensite (Weaver, 1989), may also formed during burial diagenesis usually by stripping the interlayer hydroxy sheets from discrete chlorite during weathering. In most cases it is difficult to collect a shale outcrop sample in which the chlorite has not altered to chlorite/smectite or chlorite/vermiculite. The presence of these interstratified phases is an indication of mild climatic conditions in the source area. In shales more often chlorite occurs with illite and in greenschists with muscovite-phengite. Chlorites are relatively abundant in slates.

Vermiculites occur in variable amounts in most soils of temperate and subtropical climates. They are almost always the alteration products of micao and chlorite. They commonly occur as interstratified with other phyllosilicate minerals (mica/vermiculite, chlorite/vermiculite, illite/vermiculite etc). Vermiculite can be found anywhere biotite is found.

Kaolinite is considered to have formed under humid tropical and subtropical conditions. However, it has been shown that kaolinite can form in cool temperate climates with moderate rainfall (100-200 cm). In addition to a large water flux over a long period of time, to form thick kaolinite deposits, it is necessary, to have a relatively smooth terrain and quiet tectonic conditions so that chemical weathering can be more effective than erosion. Kaolinite disappears from shales during deep burial. The depth and temperature at which it disappears vary widely depending on the pH, chemistry, rock porosity and permeability and time. Commonly, kaolinite does not exist at temperatures in excess of 200° C.

Weaver (1967) studying data of clay mineralogy of about 70,000 silts and shales, found that from Tertiary to Precambrian montmorillonite and kaolinite decrease significantly while chlorite and illite increase characteristically.

The mechanisms of clay evolution during burial diagenesis differ according to sediment permeability, lithology, fluid pressure and geothermal gradient. Chamley (1989) believes that more important than geologic age are the geothermal gradient and residence time of the burried sediments.

Tsirambides (1983) and Trontsios (1991) studied in their PhD theses the mineral changes of sediments in relation to depth from drillings at the deltas of Nestos and Evros respectively. The flysch of Pindos (Fytrolakis and Mposkos, 1985), the marine and land molassic sediments of N. Greece (Lalechos, 1986) and the sediments of Serbo-Macedonian and Rhodope massifs (Chatzidimitriadis, 1990a,b) are some other relative works.

The variation of clay mineral constituents of some Greek shales and slates in relation to geologic time is studied in this paper.

## GEOLOGIC SETTING

Renz (1940) was the first who established the meaning of geotectonic zone in the Greek territory. Each geotectonic zone includes areas with similar petrographic and tectonic characteristics. Six of the areas studied belong geotectonically to the Internal Hellenides and two to the External Hellenides

(Fig. 1). The geologic and geotectonic evolution of the Internal zones was studied by Kossmat (1924), Mercier (1966/73), Dimitrievic (1974), Kockel et al. (1971), Kauffman et al. (1976), Chatzidimitriadis et al. (1985, 1990) and Chatzidimitriadis (1990a,b).

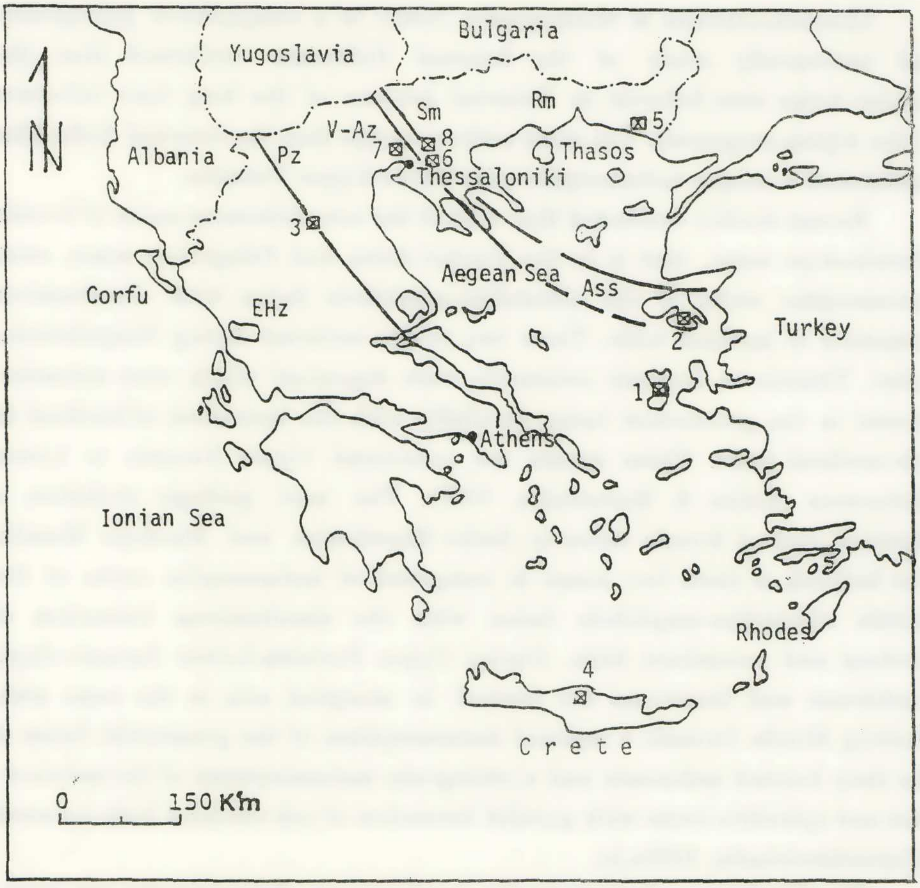



Fig. 1. Geographic and geotectonic sketch map of Greece showing the occurrence sites of shales and slates studied (☒). 1. Silurian-Devonian formations of Chios, 2. Carboniferous-Permian formations of Lesbos, 3. Permian-Triasic formations of Eratira, 4. Permian-Triassic formations of Crete, 5.Permian-Triassic formations of Makri, 6. Permian-Lower Jurassic formations of Asvestochori, 7. Upper Jurassic formations of Neochorouda, 8. Oligocene formations of Langadas. EHz = External Hellenic zones, Pz = Pelagonian zone, V - Az = Vardar - Axios zone, Sm = Serbo-Macedonian Massif, Rm = Rhodope Massif, Ass = Autochthonous series of Svoula.

The essential difference between the Internal and External Hellenides is the predominance of high grade metamorphic rocks in the first which extend from the Rhodope Massif in the east to Pelagonian zone in the west. The Alpine sedimentation is negligible in the Internal Hellenides and very extensive in the External Hellenides where the occurrence of high grade metamorphic rocks is limited.

Chatzidimitriadis & Staikopoulos (1987) in a comparative geologically and tectonically study of the Internal Hellenides confirmed that the Vardar-Axios zone behaves as External because of the long time influence of the Alpine orogenesis. The same authors accept that the Internal Hellenides constituted a unique metamorphic suite before Upper Permian.

Recent studies concluded that west of the autochthonous series of Svoula (Perirhodope zone), that is in the Vardar-Axios and Pelagonian zones, exist metamorphic rocks of the almandine-amphibole facies with simultaneous formation of isoclinal folds. These two events occurred during Neopaleozoic. Later, Triassic to Jurassic sediments were deposited which were metamorphosed in the greenschist facies parallelly with the formation of isoclinal to sub-isoclinal folds. These events are considered Upper Jurassic to Lower Cretaceous (Kilias & Mountrakis, 1987). The next geologic evolution is observed east of Svoula series in Serbo-Macedonian and Rhodope Massifs. The bedrock of these two zones is composed of metamorphic rocks of the middle almandine-amphibole facies with the simultaneous formation of isoclinal and recumbent folds. During Upper Permian-Lower Jurassic clays, sandstones and limestones are formed in marginal seas in the same area. Durring Middle Jurassic a regional metamorphism of the greenschist facies of the deep burried sediments and a retrograde metamorphism of the metamorphic and ophiolitic rocks with parallel formation of sub-isoclinal folds occurred (Chatzidimitriadis, 1990a,b).

The lithologic and stratigraphic emplacement of our samples are shown in the schematic geologic cross-sections of Figures 2 and 3.

## METHODS

Twenty one samples were collected from three island and five mainland outcrops of Greece and were analyzed in detail using petrographic and X-ray diffraction (XRD) techniques.

Thin sections of the rock samples were prepared for examination in transmitted light. Prior to XRD analysis, the samples were ground and homogenized

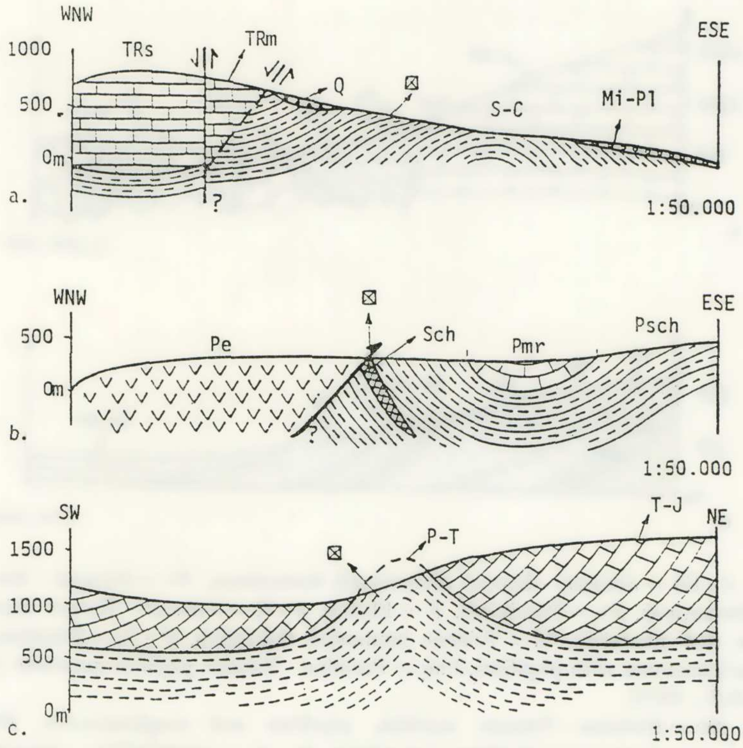
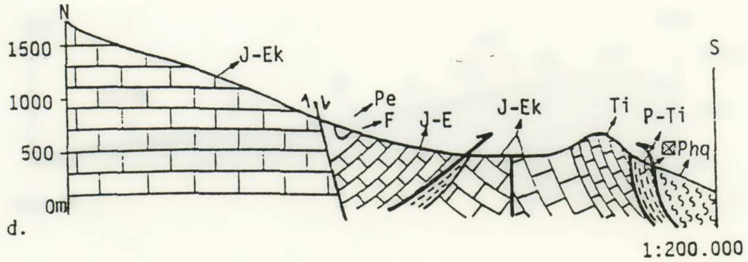
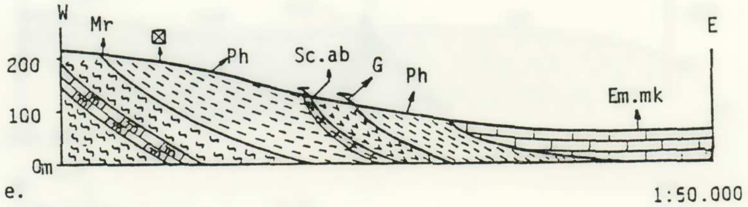



Fig. 2. Schematic geologic cross-sections and sample collection sites (⊠). a. Chios: TRs = Carnian - Jurassic limestones and dolomites, TRm = Ladinian - Carnian light colored and massive limestones, Q = Quarternary conglomerates, S-C = Silurian-Carboniferous greywackes with intercalations of conglomerates, shales and cherts, Mi-Pl = Upper Miocene-Pliocene red clays and silts (modified from I.G.S.R., 1971).
b. Lesbos: Pe = Peridodite, Sch = Late Paleozoic greenschists and metabasalts intercalated with marbles, Pmr = Permian schists and marbles, Psch = Permian phyllites and metasediments (modified from I.G.S.R., 1972).
c. Eratira: P - T = Permian - Triassic semi-metamorphic schists, T-J = Middle Triassic - Lower Liassic limestones and dolomites (modified from I.G.M.E., 1982).

in an agate mortar and were separated into two size fractions (150-20 and $<20\mu m$) by wet sieving and gravity accelaration. Subsequently, randomly and parallelly oriented mounts were prepared for XRD analysis. All the parallelly oriented mounts were reanalyzed following ethylene-glycolation to distinguish the expandable mineral phases. XRD analysis was performed using a Philips X-ray diffractometer with Ni-filtered, CuKa radiation. Semi-quantitative




d. Crete: J - Ek = Jurassic - Eocene plattenkalk formations, Pe = Jurassic - Eocene plattenkalk formations, Pe = Peridotite, F = Flysch, J - E = Jurassic - Eocene thick bedded limestones and dolomites, Ti = Triassic laminated dolomites, P - Ti = Permian - Triassic crystalline limestones with phyllites, Phq = Permian - Triassic phyllite-quartzite (modinfied from I.G.S.R., 1977).

e. Makri: Mr = Permian - Triassic marbles, phyllites and conglomerates, Ph = Upper Jurassic - Lower Cretaceous phyllites and schists, Sc. ab = amphibolitic - chloritic schists, G = Metamorphozed and schisted gabbro-microgabbro, Em. mk = Middle Eocene marly, thin-bedded limestones (modified from I.G.M.E., 1982).

estimates of the mineral abundances were made from the XRD data using the methods of Johns et al. (1954), Schultz (1964) and Perry & Hower (1970).

The grade of diagenesis or metamorphism is estimated from a sequence of 10 Å peaks showing decrease in peak width at half height (Kubler Index) according to Weaver (1984).

## RESULTS

### *Petrography*

The mega- and microscopic examination revealed that thirteen of the samples studied are discrete sedimentary rocks and the rest eight metamorphic rocks (Table 1). One arkose, three greywackes and nine medium to fine grained shales consist the sedimentary formations. Five slates and three greenschists constitute the metamorphic formations of the anchizone and epizone respectively. Precambrian and Lower Paleozoic shales have not been detected in the

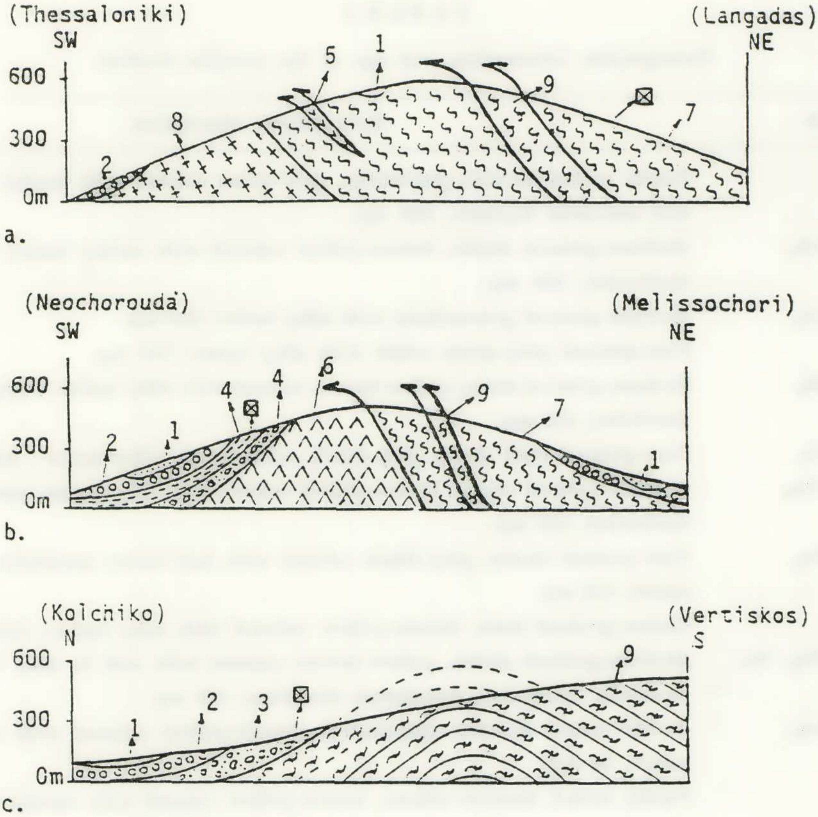



Fig. 3. Schematic geologic cross-sections and sample collection sites (⊠).
1. Pleistocene upper terrace system, 2. Upper Miocene - Pliocene terrestrial, marine and brackish deposits, 3. Lower Oligocene molasse deposits, 4. Upper Jurassic conglomerates and phyllites, 5. Upper Permian - Lower Jurassic partly serpentinized dunite-peridotite, 6. Upper Permian-Lower Jurassic uralitized gabbro, 7. Upper Permian-Lower Jurassic graphitic phyllites, sandstones and limestones, 8. Upper Carboniferous - Lower Permian greengneisses to greenschists, 9. Paleozoic ortho - and paragneisses (modified from Kockel & Mollat, 1977). a. Langadas, b. Neochorouda, c. Asvestochori. Scale 1 : 50,000.

Greek territory (except of Chios-area). Probably they have been metamorphosed to paragneisses during burial metamorphism.

The microscopic examination of thin sections revealed the following :

$Ch_1$ = Poorly sorted. Quartz, feldspars, micas (biotite + muscovite), chlorite, some opaques and rock fragments consist its constituents. Matrix >15%. Feldspars >Rock fragments.

TABLE 1

Petrographic information and age of the samples studied

| Sample | Petrographic description |
|---|---|
| $Ch_1$ | Poorly sorted massive greywacke, grey-green colored with earthy luster and concoidal fracture; 350 my. |
| $Ch_2$, $Ch_3$ | Medium-grained shales, brown-yellow colored with earthy luster; cross-laminated; 350 my. |
| $Le_1$, $Le_2$ | Medium-grained greenschists with silky luster; 310 my. |
| $Le_3$ | Fine-grained grey-green schist with silky luster; 310 my. |
| $Er_2$, $Er_3$ | Medium-grained slates, yellow-brown colored with silky luster; manganese dendrites; 240 my. |
| $Cr_1$, $Cr_2$ | Fine-grained hard slates, grey-black colored with silky luster ; 230 my. |
| $Ma_1$, $Ma_2$ | Medium-grained shales, brown-yellow colored with silky luster; parallelly laminated; 220 my. |
| $As_1$, $As_2$ | Fine-grained shales, grey-black colored with dull luster; parallelly laminated; 210 my. |
| $As_3$ | Coarse-grained slate, brown-yellow colored with silky luster; 210 my. |
| $Ne_1$, $Ne_2$, $Ne_3$ | Medium-grained shales, yellow-brown colored with dull to silky luster; parallelly laminated; manganese dendrites; 150 my. |
| $La_1$, $La_2$ | Poorly sorted massive greywackes, brown-yellow colored with earthy luster; 30 my. |
| $La_3$ | Poorly sorted massive arkose, brown-yellow colored with earthy luster; 30 my. |

$Ch_1$-$Ch_2$-$Ch_3$ = Chios, $Le_1$-$Le_2$-$Le_3$ = Lesbos, $Er_1$-$Er_2$ = Eratira Kozani, $Cr_1$-$Cr_2$ = Crete, $Ma_1$-$Ma_2$ = Makri Alexandroupolis, $As_1$-$As_2$-$As_3$ = Asvestochori Thessaloniki, Ne-$_1$Ne-$_2$Ne$_3$= Neochorouda Thessaloniki, $La_1$-$La_2$-$La_3$ = Langadas.

$Ch_2$–$Ch_3$ = Medium-grained. Quartz, feldspars, micas, chlorite and other clay minerals and some opaques are the main minerals. Predominance of muscovite among micas.

$Le_1$ = Medium-grained. Absence of quartz and feldspars. Actinolite and chlorite + sericite occur in equal amounts. Some epidote, pyroxene and opaque crystals.

$Le_2$ = Medium-grained. Absence of quartz. Actinolite, epidote, chlorite and sericite predominate. Some plagioclase, K-feldspar and opaque crystals.

$Le_3$ = Fine-grained. Quartz is the predominant phase. Absence of K-feldspar. Among phyllosilicates sericite predominates. Chlorite and calcite are present in small amounts.

$Er_1$–$Er_2$ = Medium-grained. Quartz, feldspars and micas are the predominant phases. Calcite is abundant in $Er_1$, too. Sericite predominates among micas.

$Cr_1$–$Cr_2$ = Fine-grained. Quartz, feldspars and micas (especially sericite) are the predominant phases.

$Ma_1$–$Ma_2$ = Medium-grained. Quartz, feldspars, micas and calcite are the predominant phases.

$As_1$–$As_2$ = Fine-grained. Quartz, feldspars, micas (mainly sericite) and chlorite predominate.

$As_3$ = Coarse-grained. Quartz, feldspars, micas (mainly sericite) and calcite are the main constituents.

$Ne_1$–$Ne_2$–$Ne_3$ = Medium-grained. Quartz, feldspars, calcite, micas (mainly sericite) and chlorite predominate.

$La_1$–$La_2$ = Poorly sorted. Quartz, plagioclase, calcite, micas and vermiculite are the main phases. Matrix $>15\%$.

$La_3$ = Poorly sorted. Quartz, feldspars (intensely sericitized), calcite, micas and vermiculite predominate. Matrix $<15\%$.

Further insight into the nature and abundance of the mineral constituents of the studied rock formations comes from consideration of XRD analysis.

*X-ray mineralogy*

The results of XRD analysis of the 250-20 and $<20\mu m$ size fractions of the samples studied are given in Table 2. Different minerals are concentrated in different grain sizes. Quartz, K-feldspar, plagioclase, calcite, actinolite and micas are concentrated in the coarser fraction. Fine grained muscovite (sericite and/or illite), chlorite, vermiculite, kaolinite, smectite and the interstratifications between them, predominate in the finer fraction. The interstratifications detected are mica/ smectite, illite/smectite, chlorite/ smectite and chlorite/vermiculite. The percentage of clay minerals increases with decreasing grain size. However, chlorite is more abundant in the 250-20$\mu m$ fraction. The non-clay minerals generally decrease with decreasing grain size.

TABLE 2

Mineralogical composition (%) of the samples analyzed

| Sample | Fraction (μm) | Q | Pl | Or | C | Ac | M | S | Ch | V | K |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $Ch_1$ | 250—20 | 58 | 14 | 4 | | | 12 | | 6 | | 6 |
| | <20 | 43 | 28 | 4 | | | 17(4.6)* | + | 4 | + | 4 |
| $Ch_2$ | 250—20 | 42 | 22 | | | | 19 | | 12 | | 5 |
| | <20 | 39 | 26 | | | | 24(5.4) | + | 6 | | 5 |
| $Ch_3$ | 250—20 | 43 | 24 | | | | 18 | | 9 | | 6 |
| | <20 | 41 | 32 | | | | 19(6.0) | + | 4 | | 4 |
| $Le_1$ | 250—20 | | | | | 48 | 14 | | 38 | | |
| | <20 | | | | | 45 | 12(3.2) | | 43 | | |
| $Le_2$ | 250—20 | | 25 | 13 | | 27 | 13 | | 22 | | |
| | <20 | | 15 | 13 | | 51 | 11(2.2) | | 10 | | |
| $Le_3$ | 250—20 | 69 | 4 | | 3 | | 13 | | 5 | | 6 |
| | <20 | 69 | 4 | | 3 | | 16(2.2) | | 4 | | 4 |
| $Er_1$ | 250—20 | 23 | 9 | 5 | 22 | | 29 | | 12 | | |
| | <20 | 32 | 10 | 6 | 20 | | 21(2.2) | + | 6 | | 5 |
| $Er_2$ | 250 20 | 22 | 12 | 10 | | | 35 | | 16 | | 5 |
| | <20 | 32 | 14 | 13 | | | 28(2.2) | + | 9 | | 4 |
| $Cr_1$ | 250—20 | 76 | 3 | | | | 21 | | | | |
| | <20 | 68 | 4 | | | | 28(2.0) | + | | | |
| $Cr_2$ | 250—20 | 41 | 9 | 9 | | | 23 | | 12 | | 6 |
| | <20 | 35 | 12 | 12 | | | 25(4.4) | | 12 | | 4 |
| $Ma_1$ | 250 20 | 24 | 14 | 3 | 29 | | 15 | | 6 | | 9 |
| | <20 | 26 | 8 | 4 | 39 | | 10(2.2) | | 6 | | 7 |
| $Ma_2$ | 250 20 | 17 | 3 | | 63 | | 8 | | | | 9 |
| | <20 | 11 | | | 74 | | 7(2.2) | + | | | 8 |
| $As_1$ | 250 20 | 38 | 18 | 6 | | | 16 | | 11 | | 11 |
| | <20 | 42 | 17 | 6 | | | 20(2.4) | | 8 | | 7 |
| $As_2$ | 250—20 | 31 | 22 | 13 | | | 13 | | 13 | | 8 |
| | <20 | 33 | 25 | 9 | | | 19(2.2) | | 8 | | 6 |
| $As_3$ | 250—20 | 48 | 7 | 4 | 19 | | 9 | | 8 | | 5 |
| | <20 | 43 | 6 | 4 | 21 | | 13(3.2) | | 7 | | 6 |
| $Ne_1$ | 250 20 | 19 | 4 | 3 | 50 | | 9 | | 9 | | 6 |
| | <20 | 24 | 3 | | 49 | | 10(3.8) | + | 8 | | 6 |
| $Ne_2$ | 250 20 | 19 | 4 | 3 | 39 | | 10 | | 19 | | 6 |
| | <20 | 13 | 4 | 3 | 50 | | 14(3.0) | + | 10 | | 6 |
| $Ne_3$ | 250 20 | 17 | 4 | 3 | 43 | | 9 | | 18 | | 6 |
| | <20 | 23 | 3 | | 49 | | 10(4.0) | + | 10 | | 5 |
| $La_1$ | 250 20 | 22 | 17 | | 11 | | 28 | | | 14 | 8 |
| | <20 | 14 | 11 | | 24 | | 17(14.0) | | | 23 | 11 |
| $La_2$ | 250—20 | 44 | 12 | | 6 | | 19 | | | 12 | 7 |
| | <20 | 16 | 12 | 5 | 15 | | 22(6.0) | | | 18 | 12 |
| $La_3$ | 250 20 | 19 | 26 | 11 | 16 | | 15 | | | 7 | 6 |
| | <20 | 15 | 16 | 7 | 38 | | 12(3.2) | | | 6 | 6 |

Q = quartz, Pl = plagioclase, Or = orthoclase, C = calcite, Ac = actinolite, M = mica (biotite + muscovite + sericite + illite + M/S + I/S), S = smectite, Ch = chlorite (+ Ch/S + Ch/V), V = vermiculite, K = kaolinite.

( )* Kubler Index, + = presence in minor amounts.

The XRD qualitative and semi-quantitative data are in high agreement with those from the microscopic analysis.

The Kubler Index of most of the metamorphic samples has values close to 2.0 mm. Most shale samples present K.I. values between 2.0 and 3.7 mm meaning that they have undergone late diagenesis. The rest, with values between 3.7 and 7.2 mm (Chios, Neochorouda and Langadas), have undergone middle diagenesis.

Figure 4 shows the relative abundances of the major groups of clay minerals in Phanerozoic mudrocks (generalized from Wealver, 1967). Our data are in good agreement with the mineral curves from ancient to the present, taking into account that in the illite abundances the mixed-layer mica/sme-

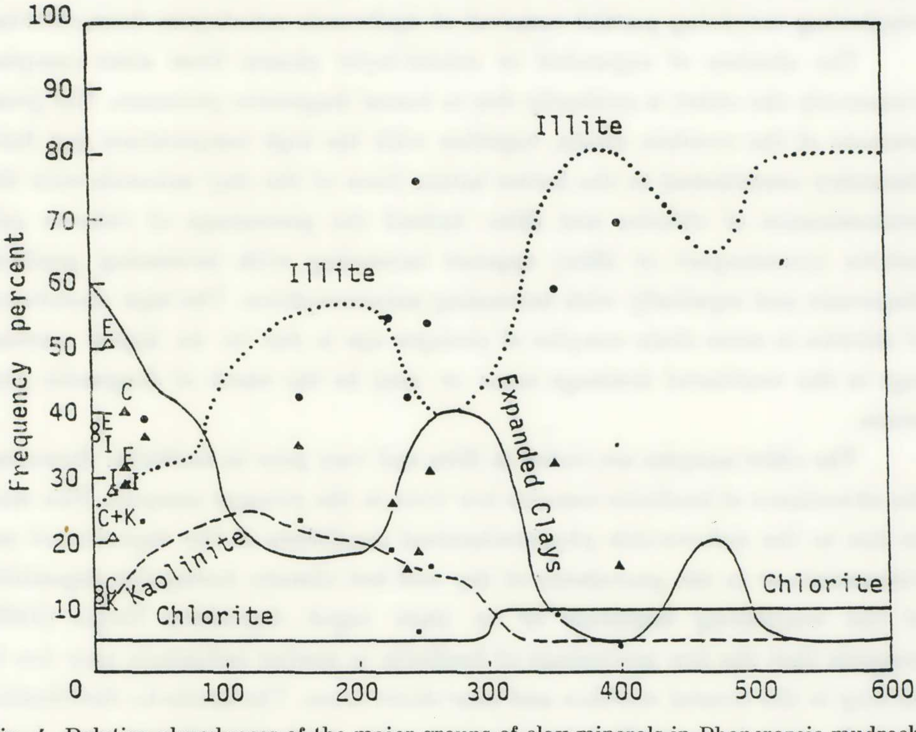



Fig. 4. Relative abundances of the major groups of clay minerals in Phanerozoic mudrocks (generalized from Weaver, 1967).

● Clay percentages in the modern ocean (Griffin et al., 1968).

▲ Clay percentages in Miocene siltstones of North Aegean (Tsirambides, 1983).

Δ Clay percentages in Upper Eocene claystones of North Aegean (Ttrontsios, 1991).

● ▲ ■ Clay percentages in this work.

E = expanded clays, I = illite, C = chlorite, K = kaolinite.

ctite and illite/smectite abundances and in the chlorite abundances the mixed layer of chlorite/smectite and chlorite/vermiculite abundances are included respectively. The clay mineral abundances of Miocene siltstones (Tsirambides, 1983) and Upper Eocene claystones (Trontsios, 1991) of North Aegean, as well as of modern ocean (Griffin et al., 1968) sediments are shown in the same Figure.

## CONCLUSIONS

The presence of vermiculite is closely related to the micas and chlorite with which it shows lattice and genetic similarities. The distinguished mixed-layer phases of chlorite/ vermiculite and chlorite/smectite may be considered degradation products of discrete chlorite. They were probably formed by weathering involving partial removal of hydroxide interlayers from chlorite.

The absence of expanded or mixed-layer phases from some samples (commonly the older) is evidently due to burial diagenetic processes. The great pressure of the overlain strata, together with the high temperature and fluid chemistry contributed to the better lattice form of the clay minerals with the predominance of chlorite and illite. Indeed the percentage of chlorite and sericite (counterpart of illite) appears increasing with increasing grade of diagenesis and especially with increasing metamorphism. The high abundance of chlorite in some shale samples of younger age is due to its higher percentage in the weathered drainage areas or may be the result of diagenetic processes.

The older samples are richer in illite and very poor in kaolinite. However, the abundance of kaolinite remains low even in the younger samples. This may be due to the unfavorable physicochemical conditions in the depositional environments or to the prevalence of dry and hot climate during the deposition of the weathering materials or to their rapid deposition Tröger (1969) suggests that the low percentage of kaolinite in marine sediments may due to its trap in the coastal marshes and near-shore areas. The kaolinite distribution in such areas is controlled by strong marine currents and rising sea level. Another reason of low kaolinite content in most of our samples is the high carbonate content of the adjacent parent rocks, which is the result of shallow marine sedimentation in older geologic times.

Hydrothermal alteration of parent rocks is missing from all eight areas studied. The organic content, especially in the younger less indurated samples, is negligible. This fact means that the sedimentation took place in high Eh environments.

Diagenetic mineral islands inside slates and phyllites are very common. In this case the carbonization of the organic material acts as insulator degrading thus the P, T conditions during epizonic metamorphism. Permian — Triassic clay formations rich in organics may be characterized as graphitic shales. However, the absence of this index mineral from our rocks may mean epizonic metamorphism (greenschist facies).

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## Π Ε Ρ Ι Λ Η Ψ Η

**Ἀφθονία ἀργιλικῶν ὀρυκτῶν σὲ σχιστοπηλοὺς καὶ ἀργιλικοὺς σχιστολίθους ἀπὸ ὁρισμένες περιοχὲς τοῦ Ἑλληνικοῦ χώρου διὰ μέσου τοῦ γεωλογικοῦ χρόνου**

Σ κ ο π ό ς: Στὴν ἐργασία αὐτὴ ἐξετάζονται ὁρισμένα ἐπιφανειακὰ πετρώματα ἀπὸ νησιωτικὲς καὶ ἠπειρωτικὲς περιοχὲς τῆς Ἑλλάδας μὲ βάση:

α. Τὴν ποιοτικὴ καὶ ποσοτικὴ διαφοροποίηση τῶν ἀργιλικῶν καὶ μὴ ὀρυκτῶν συστατικῶν τῶν πετρωμάτων ποὺ ἀναλύονται κατὰ κοκκομετρικὸ κλάσμα καὶ ἡλικία.

β. Τὴν ἐκτίμηση τοῦ βαθμοῦ διαγένεσης καὶ ἀγχιμεταμόρφωσης ποὺ ἔχουν ὑποστεῖ αὐτὰ τὰ πετρώματα μὲ τὴν ἐπίδραση φυσικοχημικῶν παραγόντων καὶ τοῦ γεωλογικοῦ χρόνου.

Διδακτορικὲς διατριβὲς ἔχουν ἀσχοληθεῖ λεπτομερῶς μὲ τὶς ὀρυκτολογικὲς μετατροπὲς ἰζημάτων σὲ σχέση μὲ τὸ βάθος, ἐξετάζοντας δείγματα γεωτρήσεων στὰ δέλτα τῶν ποταμῶν Νέστου (Τσιραμπίδης, 1983) καὶ Ἕβρου (Τρώντσιος, 1991). Ἐπίσης, εἰδικὲς μελέτες ἔχουν γίνει γιὰ τὸ φλύσχη τῆς Πίνδου (Φυτρολάκης καὶ Μπόσκος, 1985), τὰ θαλάσσια καὶ ἠπειρωτικὰ μολασσικὰ ἰζήματα τῆς Β. Ἑλλάδας (Λαλεχός, 1986) καὶ τὰ ἰζήματα τῆς Σερβο-Μακεδονικῆς μάζας καὶ τῆς μάζας τῆς Ροδόπης (Χατζηδημητριάδης, 1990a,b).

Σκοπὸς τῆς ἐργασίας αὐτῆς εἶναι ἡ ἐκτίμηση τῶν παλαιοκλιματικῶν συνθηκῶν κάτω ἀπὸ τὶς ὁποῖες συνέβησαν οἱ ὀρυκτολογικὲς μετατροπὲς καὶ ὁ σχηματισμὸς τῶν πετρωμάτων ποὺ ἐξετάζονται καὶ ποὺ σήμερα βρίσκονται στὴν ἐπιφάνεια.

Μ έ θ ο δ ο ι: Συλλέχθηκαν εἴκοσι ἕνα δείγματα διαφορετικῆς ἡλικίας ἀπὸ τρεῖς νησιωτικὲς καὶ πέντε ἠπειρωτικὲς ἐμφανίσεις καὶ ἀναλύθηκαν λεπτομερῶς πετρογραφικὰ καὶ ἀκτινογραφικά. Ἑτοιμάστηκαν λεπτὲς τομὲς γιὰ μικροσκοπικὴ ἐξέταση καὶ μέρη τῶν δειγμάτων κονιοποιήθηκαν και ὁμογενοποιήθηκαν σὲ ἀχάτινο γουδὶ καὶ στὴ συνέχεια διαχωρίστηκαν σὲ δύο κλάσματα (250-20 καὶ < 20 μικρὰ) μὲ κοσκίνιση καὶ φυγοκέντριση. Εἰδικὰ παρασκευάσματά τους ἀκτινογραφήθηκαν σὲ περιθλασίμετρο καὶ ἔγινε ποσοτικὴ ἐκτίμηση τῶν ὀρυκτῶν συστατικῶν τους. Τέλος, προσδιορίστηκε ὁ βαθμὸς διαγένεσης καὶ μεταμόρφωσης ὅλων τῶν δειγμάτων μὲ βάση τὴν ἐργασία τοῦ Weaver (1984).

Ἀποτελέσματα: Ἡ μακρο- καὶ μικροσκοπικὴ ἐξέταση ἀποκάλυψε ὅτι δέκα τρία δείγματα εἶναι ἀμιγῆ ἰζηματογενῆ πετρώματα καὶ τὰ ὑπόλοιπα ὀκτὼ μεταμορφωμένα. Ἕνας ἀρκόζης, τρεῖς γραουβάκες καὶ ἐννέα μεσόκοκκοι μέχρι λεπτόκοκκοι σχιστοπηλοὶ ἀποτελοῦν τοὺς ἰζηματογενεῖς σχηματισμούς. Πέντε ἀργιλικοὶ σχιστόλιθοι καὶ τρεῖς πρασινοσχιστόλιθοι ἀποτελοῦν τοὺς μεταμορφωμένους σχηματισμοὺς τῆς ἀγχιζώνης καὶ ἐπιζώνης ἀντίστοιχα. Ὁ δείκτης Kubler τῶν περισσοτέρων δειγμάτων μεταμορφωμένων πετρωμάτων ἔχει τιμὲς κοντὰ στὸ 2,0 mm. Τὰ περισσότερα δείγματα σχιστοπηλῶν παρουσιάζουν τιμὲς δεικτῶν Kubler μεταξὺ 2,0 καὶ 3,7 mm, γεγονὸς ποὺ σημαίνει ὅτι ἔχουν ὑποστεῖ ὑψηλοῦ βαθμοῦ διαγένεση. Τὰ ὑπόλοιπα δείγματα μὲ τιμὲς μεταξὺ 3,7 καὶ 7,2 mm ἔχουν ὑποστεῖ μέσου βαθμοῦ διαγένεση. (Ἐκτὸς τῆς Χίου). Σχιστοπηλοί, Προκάμβριας καὶ Κάτω Παλαιοζωϊκῆς ἡλικίας δὲν ἔχουν ἐντοπιστεῖ στὴν Ἑλληνικὴ ἐπικράτεια. Προφανῶς ἔχουν μεταμορφωθεῖ σὲ παραγνευσίους κατὰ τὴ διάρκεια τῆς βυθισματογενοῦς μεταμόρφωσης.

Διαφορετικὰ ὀρυκτὰ εἶναι συγκεντρωμένα στὰ δύο κλάσματα. Χαλαζίας, καλιοῦχοι ἄστριοι, πλαγιόκλαστα, ἀσβεστίτης, ἀκτινόλιθος καὶ μαρμαρυγίες ἐπικρατοῦν στὸ ἀδρομερέστερο κλάσμα. Σερικίτης. ἰλλίτης, χλωρίτης, βερμικουλίτης, καολινίτης, σμεκτίτης, καὶ οἱ ἐνδοστρωματωμένες φάσεις μεταξὺ αὐτῶν ἐπικρατοῦν στὸ λεπτομερέστερο κλάσμα. Ἡ συμμετοχὴ τῶν ἀργιλικῶν ὀρυκτῶν αὐξάνει μὲ μείωση τοῦ μεγέθους τῶν κόκκων. Ἀπεναντίας, ὁ χλωρίτης εἶναι ἀφθονότερος, στὸ κλάσμα 250-20 μικρά.

Συμπεράσματα: Ἡ παρουσία τοῦ βερμικουλίτη σχετίζεται στενὰ μὲ τοὺς μαρμαρυγίες καὶ τὸ χλωρίτη, ὀρυκτὰ μὲ τὰ ὁποῖα μοιάζει γενετικὰ καὶ πλεγματικά. Οἱ ἐνδοστρωματωμένες φάσεις χλωρίτη/βερμικουλίτη καὶ χλωρίτη/σμεκτίτη θεωροῦνται προϊόντα ὑποβάθμισης ἀμιγοῦς χλωρίτη. Πιθανῶς σχηματίστηκαν ἀπὸ ἀποσάθρωση χλωρίτη.

Ἡ ἀπουσία ἐπεκτεινόμενων ἢ ἐνδοστρωματωμένων φάσεων ἀπὸ μερικὰ δείγματα (συνήθως τὰ παλαιότερα) πιθανῶς ὀφείλεται σὲ βυθισματογενεῖς διαγενετικὲς διεργασίες Ἡ ὑψηλὴ πίεση τῶν ὑπερκείμενων στρωμάτων μαζὶ μὲ τὴν ὑψηλὴ θερμοκρασία καὶ τὴ χημικὴ σύσταση τῶν κυκλοφορούντων διαλυμάτων εἶχαν σὰν ἀποτέλεσμα τὴν πληρέστερη δόμηση τῶν ἀργιλικῶν ὀρυκτῶν μὲ ἐπικράτηση τῶν σταθερῶν μελῶν χλωρίτη καὶ ἰλλίτη. Ἡ ἀναλογία τοῦ χλωρίτη καὶ τοῦ σερικίτη (πανομοιότυπος τοῦ ἰλλίτη) αὐξάνει μὲ αὔξηση τοῦ βαθμοῦ διαγένεσης καὶ κυρίως τοῦ βαθμοῦ μεταμόρφωσης. Ἡ μεγάλη ἀφθονία χλωρίτη σὲ μερικοὺς σχιστοπηλοὺς νεώτερης ἡλικίας ὀφείλεται στὴ μεγαλύτερη συμμετοχή του στὶς διαβρούμενες λεκάνες ἀπορροῆς ἢ μπορεῖ νὰ εἶναι ἀποτέλεσμα διαγενετικῶν διεργασιῶν.

Τέλος, διαπιστώθηκε ὅτι τὰ παλαιότερης ἡλικίας δείγματα εἶναι πλουσιότερα σὲ ἰλλίτη καὶ πολὺ πτωχὰ σὲ καολινίτη. Ἡ ἀφθονία ὅμως τοῦ καολινίτη παραμένει χαμηλὴ ἀκόμη καὶ στὰ νεώτερα δείγματα. Αὐτὸ μπορεῖ νὰ ὀφείλεται σὲ δυσμενεῖς φυσικοχημικὲς συνθῆκες στὰ ἀποθετικὰ περιβάλλοντα ἢ στὴν ἐπικράτηση ὑγροῦ καὶ θερμοῦ κλίματος κατὰ τὴ διάρκεια τῆς ἀπόθεσης τῶν ὑλικῶν ἀποσάθρωσης ἢ τέλος στὴ ραγδαία τους ἀπόθεση. Ἕνα ἄλλο αἴτιο τοῦ χαμηλοῦ περιεχομένου σὲ καολινίτη στὰ περισσότερα ἀπὸ τὰ δείγματά μας εἶναι ἡ μεγάλη ἀφθονία τῶν ἀνθρακικῶν πετρωμάτων στὶς γειτονικὲς περιοχές, ποὺ εἶναι ἀποτέλεσμα ρηχῆς θαλάσσιας ἰζηματογένεσης σὲ παλαιότερες γεωλογικὲς ἐποχές.

Ὑδροθερμικὴ ἐξαλλοίωση τῶν μητρικῶν πετρωμάτων δὲν παρατηρήθηκε σὲ καμμία ἀπὸ τὶς ὀκτὼ περιοχὲς μελέτης. Ἀκόμη, τὸ περιεχόμενο σὲ ὀργανικὴ ὕλη ὅλων τῶν δειγμάτων καὶ ἰδιαίτερα τῶν νεώτερων καὶ λιγότερο ἀποσκληρωμένων εἶναι ἀσήμαντο, γεγονὸς ποὺ σημαίνει ὅτι ἡ ἰζηματογένεση ἔγινε σὲ περιβάλλοντα μὲ ὑψηλὸ δυναμικὸ ὀξείδωσης.