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MIXED-LAYERED ILLITE/SMECTITE - A KEY TO UNDERSTANDING THE EVOLUTION OF FOCŞANI BASIN (ROMANIA)

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Abstract: Since their discovery, the phyllosilicate superstructures, known for decades as mixed-layered clay minerals, have had various applications in mineralogy, petrology, oil industry, etc. The most important and handy application of the mixed-layered illite-smectite (i/s) is modeling the evolution of the interlayer structures during burial depth. To this goal, X-ray diffraction patterns of clay association is analyzed for discreet phase identification and mixed-layered order evaluation.
This paper presents an analysis of a complete sedimentary deposit stretched between Miocene and Pliocene (5-8 Ma provided by two Valleys (Putna and Râmnicu Sărat) in the Focşani Basin aiming to solve a controversy concerning whether or not the sedimentary sequence was buried to the thickness it suggests (8,000 m). The sedimentary sequence in the Focsani Basin has been extensively analyzed in the last twenty years, aiming to discover the dynamics of this complex structure affected by active subduction and seismicity. The clay minerals analysis was focused on X-ray diffraction patterns of <2µm fraction of 250 samples and the *R* factor of the I/S ordering determined by using Środoń methods (1980 and 1984). The illite-smectite interlayer analysis showed no illitization and no ordering tendencies of the superstructures with growing thickness of the sediment which was correlated with the burial depth. The conclusion of this study does not only reveal valuable information about the evolution of the Focșani Basin but also highlights the importance of phyllosilicate superstructure analysis for understanding the complex regional dynamics.

Key words: clay minerals, Focşani Basin, mixed layered illite/smectite, x-ray diffraction.

1. INTRODUCTION

Clay mineralogy provides information for several domains, such as the sedimentary basin evolution, burial diagenesis, clastic sediments source area, hydrocarbon material dynamics and evolution, paleoclimatic changes, which can be interpreted depending on the geological context (Burst, 1959, 1969; Weaver, 1957, 1959; Perry & Hower, 1970; Hower et al., 1976; Środoń, 1978, 1984; Boles & Francks, 1979; Velde et al., 1986; etc.). The common clay association in a sedimentary lutitic fraction includes terms of sheet-silicate groups, most of all illite, smectite, kaolinite, vermiculite and chlorite as well as superstructures of their structural layers, usually named interstratifications (or mixed-layered). The expandable layers are the most important to consider, the most common being a smectite term, montmorillonite or, in some cases, vermiculite. The extension of the expandable layers and their ordering in a superstructure are considered markers for burial diagenesis of the clay sediments.

There seems to be a general agreement on the evolution of the mixed layer, regardless of the type of layers in a superstructure, namely that there is a tendency for all interstratifications to evolve from imperfect, metastable arrangements to orderly, homogeneous, defect free arrangements and these changes are driven by increased temperature and pressure levels (Moore & Reynolds, 1997). For the understanding of the transition mechanism, two models were proposed: *the MacEwan crystallite model* (MacEwan & Wilson, 1980) and *the fundamental particle model* (Nadeau, et al, 1984). *The MacEwan crystallite model* considers illite and smectite interlayered in a regular or irregular sequence and the division between layers through the center of the octahedral sheet. In such a case, the evolution of the superstructure to ordered illite/smectite interlayer is produced by solid state transformation. *The* *fundamental particle model* divides the layers at the interlayer space and the particles are not grown together epitaxially, but are rather simply stacked in a sequence that acts as a unitary diffracting unit for X-rays. But one model does not exclude the other and a transition illite/smectite mediated by interlayers can integrate both models, especially into complex systems involving both burial and tectonic deformation. The transition mechanism is still being debated and it seems to be related to the permeability of the system and the water availability for mediating the transition. Another subject of the dispute is about whether I/S is one phase, or two phases, or several, but that depends on the transition mechanism we consider: if I/S is an intermediate term in the solid state transformation illite-smectite, it may be considered an "intermediate term" in a solid solution; if it is a polytypism as a particular case of polymorphism, it may be a polymorphic phase.

Reynolds & Hower (1970) proposed a method for describing illite/smectite interstratifications and they considered 3 types of illite and smectite layers distribution in a sheet silicate superstructure: random (*R*), *IS-ordered* and *ISII-ordered*, with *I* – illite layer and *S* – smectite layer. Środoń (1981, 1984) proposed a method using $d_{(001)}$, $d_{(002)}$, $d_{(003)}$ XRD peak position of illite and air-dry and ethylene glycol-solvated smectite for the interstratifications indexing. This paper is based on this approach.

The Focşani zone, located in front of the Eastern Carpathians, is a foredeep basin with 10 kilometers thickness deposits (Tărăpoancă et al., 2003) and the clay mineralogy was investigated in a section covering Upper Miocene to Quaternary deposits. The sequence enfold a seismically active area, affected by a rapid subsidence. The Carpathian region active subduction ceased about 9 Ma but the final phase of oceanic lithosphere subduction and detachment still produces seismicity and subsidence. The Upper Miocene to Pliocene sequence in the Focşani foredeep basin contains shallow marine to shallow lacustrine sedimentary deposits. The petrographic and geochemical analysis of these deposits suggests that the source area is the East Carpathians (in the lower part of the section), imposed by the input of the volcanic fragments with an increase of metamorphic and sedimentary elements (provided by the uplift and erosion) occurred in the nappe systems of the East Carpathian belt (Panaiotu et al., 2007, Fig. 1).

The knowledge of the Focsani basin dynamics requires clay mineralogy analysis since the presence of clay minerals in a sedimentary sequence has ultimately tectonic significance, being related to the evolution of the source area and the sedimentary basin dynamics. In this regard there were selected Putna and Râmnicu Sărat valleys open sections, located in the western part of the Focşani basin (Fig. 1), as the deposits are arranged almost vertically, allowing continuous sampling. The superposition of these two sections covers the time interval between the Upper Sarmatian to Romanian and a 10,000 m thick sequence. For revealing the evolution of the Focşani basin the clay minerals were investigated in order to determine the quantitative proportion of the phyllosilicates and their superstructure ordering.

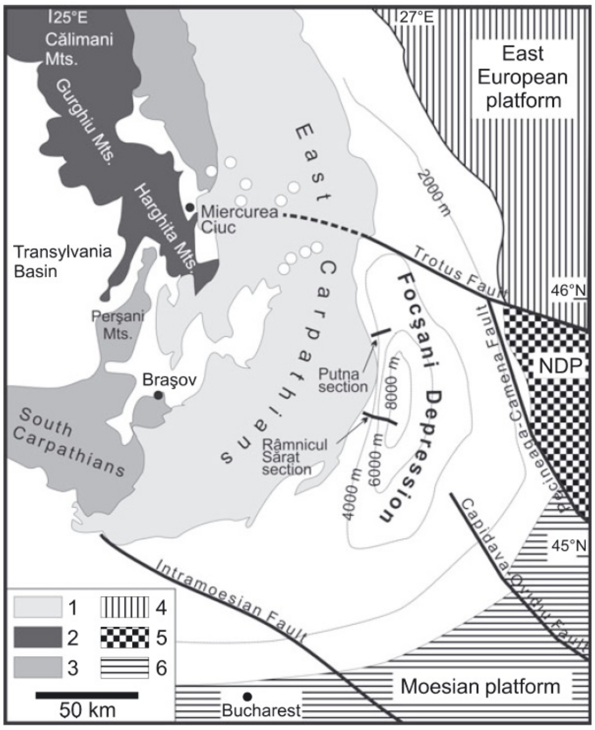

Figure 1. The location of the two section, Putna and Râmnicu Sărat and the position of the Focsşani foredeep basin (Focşani Depression on the map) on geological map. 1. East Carpathians Cretaceous–Tertiary nappe system; 2. Neogene-Quaternary volcanic arc; 3. Crystalline basement and its Mesozoic cover; 4. East European Platform; 5. North Dobrogean Promontory; 6. Moesian Platform; white dots - sampling areas for potential sources (40 samples), labelled isolines - isobaths in metres at the base of Neogene (after Dumitrescu & Săndulescu, 1970 and Panaiotu et al., 2007).

2. SAMPLE MATERIAL

A number of 164 samples were selected in order to identify the evolution of the Focşani sedimentary basin.

The Putna Valley section has a length of about 2.3 km and 70 samples were considered as covering Upper Sarmatian - Meoţian. Throughout the entire section of the Putna Valley the deposits are sub-vertical, the inclination ranging between 85° and 95°.

The Râmnicu Sărat Valley section has a length of about 7.3 km and 94 samples were considered for the clay fraction analysis. This sequence covers a time between the Meoţian and the Romanian and the deposit inclination ranges from vertical (~ 90°) to 20° E.

These sections consist in the lower part (Upper Sarmatian–Meotian) of the alternating shallow marine sandstones and shales (Panaiotu et al., 2007) and in the upper part (Pontian–Dacian–Romanian) of the brackish to lacustrine deltaic shales, siltstones, sandstones and coals (Grasu et al., 1999). Panaiotu et al., (2007) unfolded a sampling in the adjacent area (white dots on the map) for identifying the source area of the clastic material described in the two sections (Putna and Ramnicu Sărat) mentioned above. The 164 samples were subjected to a layer-silicate analysis in <2μm fraction.

3. METHODS

Clay mineralogy and mixed-layered superstructures were identified by using powder X-ray diffraction both on natural and treated samples on the following conditions: CuK_α radiation, step size 0.01 ° 2θ, step time 1s/step, scan range 3 ÷ 73 ° 2θ for natural samples and 3 ÷ 33 ° 2θ for treated samples, using a θ-θ Bragg-Brentano geometry PANalytical diffractometer.

To obtain accurate diffraction data and to avoid mineral phase interference, several treatments were applied in order to remove carbonates, organic matter and well-defined diffraction phases such as quartz and feldspar, which overlay clay minerals. Organic matter was removed by using 10% hydrogen peroxide (method Kunze & Dixon, 1986) by successive additions until the total removal of organic matter and carbonate removal was achieved by repeated treatment with acetic acid 1M Na acetate solution with pH adjusted to 4.5. (Rabenhorst & Wilding, 1984). Fraction <2μm was separated by repeated centrifugation (Negreanu et al, 2018).

Standard treatments were applied for highlighting layer-silicate species: saturation in cations (Mg^{2+} and K^+), ethylene glycol solvation and thermal treatment (330°C and 500°C). The X-ray diffraction was performed on oriented samples and diffraction data were analyzed by using the software HighScore (ICDD) and NEWMOD (Reynolds, 1985).

The chemical (K_2O) data were obtained by X-ray fluorescence on untreated samples, using Bruker-AXS spectrometer with rhodium (Rh) standard anode, from University of Utrecht, The Netherlands. The samples were irradiated with a generator setting of 60 kV in order to identify both heavy and light elements.

4. RESULTS

In the entire length of the lithological column, the <2μm fraction is dominated by expandable clay phases smectite and/or vermiculite, illite rarely becoming prevalent (Fig. 2). Additionally to these three main phases, kaolinite, present in varying proportions, chlorite and interstratified superstructures (I/S) were identified. Non-clay minerals are almost always present in low proportion and usually these are quartz, alkali-feldspars and/or plagioclase, jarosite and rarely clinoptilolite, as secondary phase of volcanic glass transformation.

The clay minerals were identified by using the combined information obtained by X-ray diffraction on treated samples.

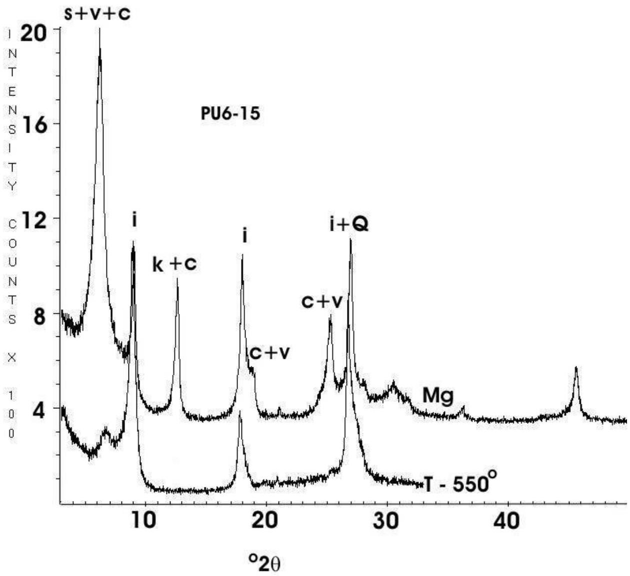

Figure 2. X-ray diffraction of treated <2μm fraction of a sample from Putna section; (s=smectite, v=vermiculite, i=illite, k=kaolinite, c=chlorite, Q=quartz).

Mixed-layered illite / smectite

Środoń (1981, 1984) and Reynolds & Hower (1970) models were used to identify and index illite and smectite discreet phases and mixed-layered ordering. The main problems encountered in describing the interstratifications were (1) mineralogical association of all three components, namely I/S interstratifications with illite and smectite discrete phases (and/or vermiculite) and (2) quartz and feldspar still present in some samples which overlap clay phases (and masking the *(060) reflections*).

Based on the samples examined the coexistence of three types of illite material was evinced: illite, as a discrete phase (no expandable layers), IS and ISII interstratifications, smectite being always present as a discrete phase. Two methods were used in order to identify the type and ordering of illite/smectite interstratifications: Środoń (1981) for describing the illite material, with 40-100% expandable layers and illite as a discrete phase, and Środoń (1984) for describing a material with 5-50% expandable layers.

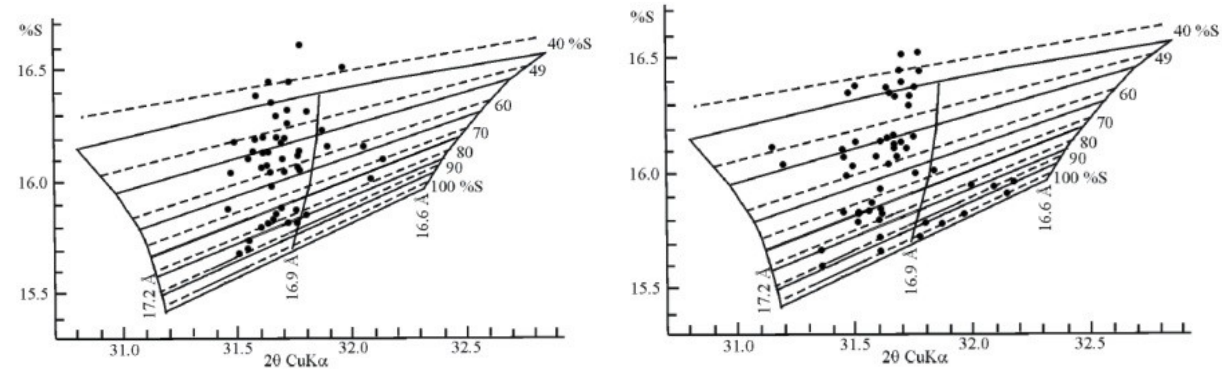

Figure 3. 15÷16 and 31÷32 °2θ peak area projection of Putna (left) and Râmnicu Sărat (right) samples using Środoń (1981) diagram.

Thus, there were considered the reflections positions (001), (002) and (003) of illite, expressed in °2θ (Środoń, 1984) and the reflections of the following areas: 15 - 16° 2θ and 31 - 32° 2θ (Środoń, 1981). Illite with no expandable layers (points in the illite "pure" area) are depicted above the theoretical lines drawn with *7-14 ÷ ∞ notation* representing the number of illite layers in a crystallite.

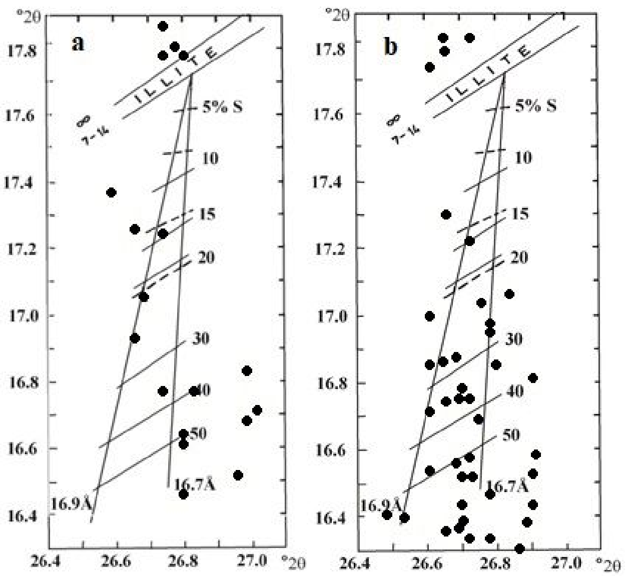

Figure 4. Peak position distribution of the area 16.4-17.8 şi 26.4-27.0 °2θ (XRD data) of Putna *(a)* and Râmnicu Sărat *(b)* using Środoń (1984) diagram.

An empirical factor $\Delta_{(002)\text{-}(001)}$ was also used for describing the ordering degree of interstratifications, as function of smectite concentration. The projection of data in Środoń diagrams (1980, 1981, 1984) is shown in Figs. 3 and 4. A $\Delta_{(002)\text{-}(001)}$ <8.7 shows poor ordering of I/S interstratification and $\Delta_{(002)\text{-}(001)}$ between 8.85 ÷ 9 shows a superior type of ordering or an association of type I + ISII (Środoń, 1984). The distribution of Δ points is presented in Fig. 5, along with smectite concentration and 15 - 16° 2θ and 31 - 32° 2θ area position variation in the composed Putna - Râmnicu Sărat section.

5. DISCUSSION

The mixed-layered I/S are present in almost all sedimentary clastic deposits and their ordering and composition provide information about their burial depth, sedimentary rate and basin dynamics. It has been proved that I/S ordering and composition evolve during burial diagenesis through increasing order of illite and smectite layers and smectite layers decline but, in this case, things are not that simple. Fig. 5 contains smectite variation concentration in the sequence and °2θ positions of the considered peaks as indication of I/S ordering. Both diagrams show neither ordering tendencies, nor a coherent variation of smectite concentration in I/S mixed-layered, consistent with a burial diagenesis evolution of sheet-silicates interstratifications.

The projection of the entire sequence Putna-Ramnicu Sarat correlated with magnetostratigraphy ages (Vasiliev et al., 2004) produced a slightly inverse illite/smectite distribution, mainly after 5 Ma, but this behavior is correlated rather with the source area shifting than with the smectite/illite transitions.

The four diagrams in Fig.5 represent different points of view regarding the expandable layers evolution in the whole sequence of Focsani Basin. The smectite concentration in I/S interstratifications shows large variability in 8000 m thickness (Fig. 5a). The 31-32° 2θ peak positions (ethylene glycol-treated samples) are restricted in the area 31.5-32°2θ in the whole sequence (near the 16.9 line in Fig. 4a, b, which represents the thickness of the ethylene glycol-smectite complex in diagenetic I/S interstratifications).

At angles bigger than 32 the expandable layer thickness decreases. The 15-16°2θ peak positions are restricted into this value, the migration to 17°2θ being characteristic to “pure” illite (Fig. 5b). The discrete distribution is again random, with no tendency to

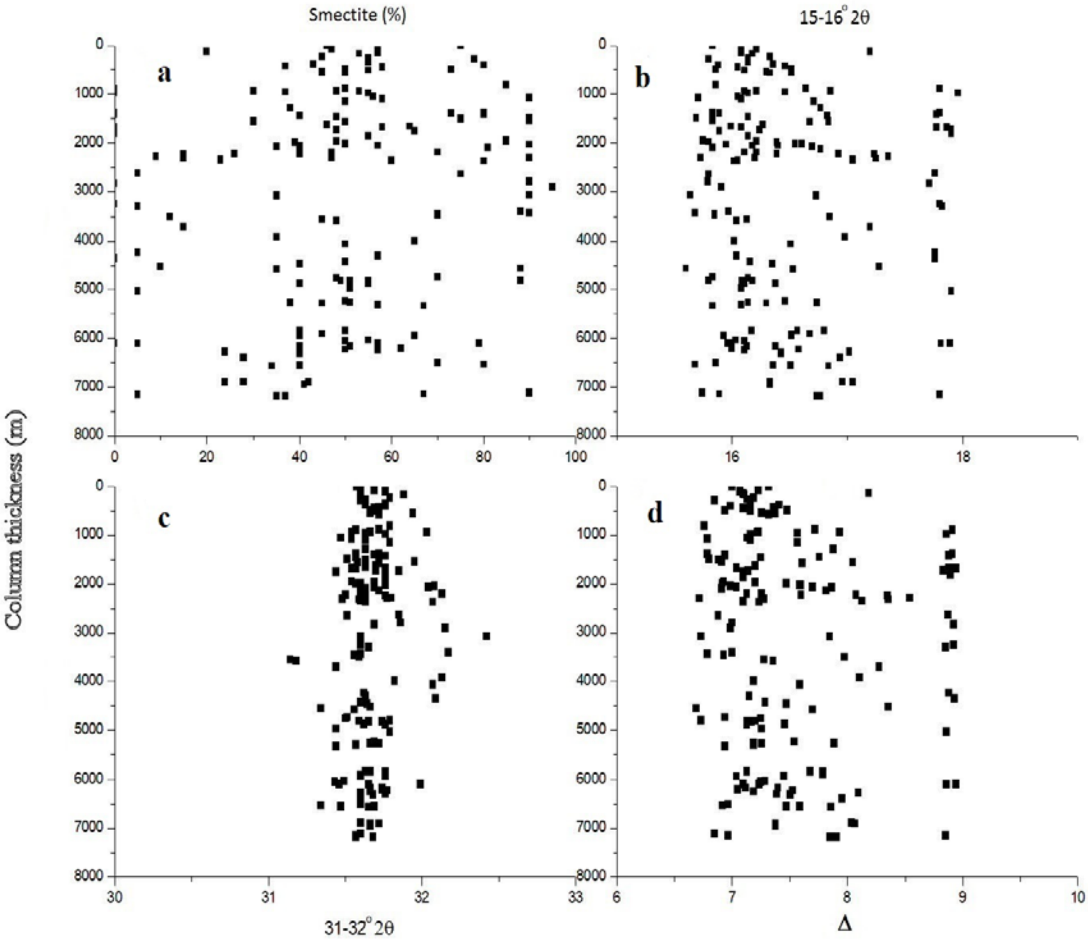

Figure 5. The vertical distribution of 15÷16 şi 31÷32 °2θ peak area (XRD data) and **Δ** factor correlated with smectite concentration in cumulated Putna - Râmnicu Sărat section ([a] - the smectite concentration in I/S interstratifications; [b] - the 15-16°2θ peak positions; [c] - the 31-32° 2θ peak positions (EG-treated samples); [d] - the Δ factor is the angle distance between (001) and (002) peak positions (the smaller the difference means more expandable layers).

gather to a more illitic composition with depth growing. The Δ factor (Fig. 5d) represents the angle distance between (001) and (002) peak positions, and the smaller the difference means more expandable layers. The diagram suggests a perfect randomness, no decreasing tendency of expandable layers with depth, the reasonable path to interstratification illitization, regardless of the transition mechanism being considered.

Thus the 8,000 m thick sequence of the Focsani Basin shows no tendency of illitization with depth, consistent with the evolution models of illite-smectite superstructures during burial diagenesis. The major factors involved in this transition, beyond the mechanisms are: K^+ availability in the system, temperature, pressure, burial rate and smectite dehydration. It is considered that smectite illitization during burial diagenesis is one of the most important reactions that may influence the evolution and dynamics of fluids in sedimentary systems. This reaction releases a large amount of H_2O in the pore space and may cause anomalous pressures in the sedimentary column (Koster van Groos & Guggenheim, 1989). Illitization does not occur if the pore fluid composition is not found in the stability field of illite (Sass et al., 1987) or if the K^+ concentration is very low, both in solution and in mineralogical association. Otherwise, illitisation may occur at fairly low temperatures (~ 70°C) and in a reaction time of ~ 300,000 years (Sass et al., 1987; Środoń & Eberl 1984). After Perry & Hower (1970) and Huang (1992) illite act as a buffer for K^+ in most of the natural sedimentary systems and, with available K^+, the illitization occurs between 70 and 130°C.

The projection of the whole sequence Putna-Ramnicu Sarat correlated with magnetostratigraphy ages (Vasiliev et al., 2004) produced a slightly inverse illite/smectite distribution (Fig. 6), mainly after 5 Ma, but this behavior is correlated rather with source area shifting then the smectite/illite transitions. K_2O concentration in the samples obtained by X-ray fluorescence on untreated samples confirms the continuous availability of K^+ in the whole sequence (Fig. 7). Previous studies (Panaiotu et al., 2007) have highlighted the presence of the K-feldspar in the entire sequence. In the lower part (8-5 Ma) clinoptilolite was also present and in the upper part (5-2 Ma), the microcline was frequent, in different stages of transformation.

The Focsani Basin evolved in an area with pronounced subsidence (subduction) and the sedimentary deposits undergo a sharp and relatively rapid burial. Despite of the inverse correlation of the illite and smectite concentration in the column (Fig. 7) and the constant K^+ availability in the system, the illitization did not occur. This lack of the smectite-illite phase transformation might be a consequence of the thermodynamic factors but rather the tectonic dynamic in the area.

6. CONCLUSIONS

This lack of smectite-illite phase transformation could have been a consequence of thermodynamic factors, however in this case, it is rather caused by the tectonic dynamics of the area. The absence of I/S illitization with depth brings more information about the depositional environment and post-depositional undergoing processes in the Focsani Basin.

The factors that govern the thermodynamic models have already been exposed, but the regional dynamics of the basin has always been the determining factor in the mineralogical evolution. Experimental studies have shown that the minimal transition temperature of smectite-illite is 150-200°C at a pressure of 1 kbar (~1 km burial depth). The sedimentary sequence has a total length of 11 km, which should have met the conditions for the illite-smectite transition that nevertheless did not take place.

In the recent decades, there have been numerous studies on the dynamics of the Carpathian-Panonic system, including the Panonic Basin and the Transylvanian and Eastern Alps, the Carpathians and the Dinars. The enclosure of the Tethys Ocean, following the collision of the African and European

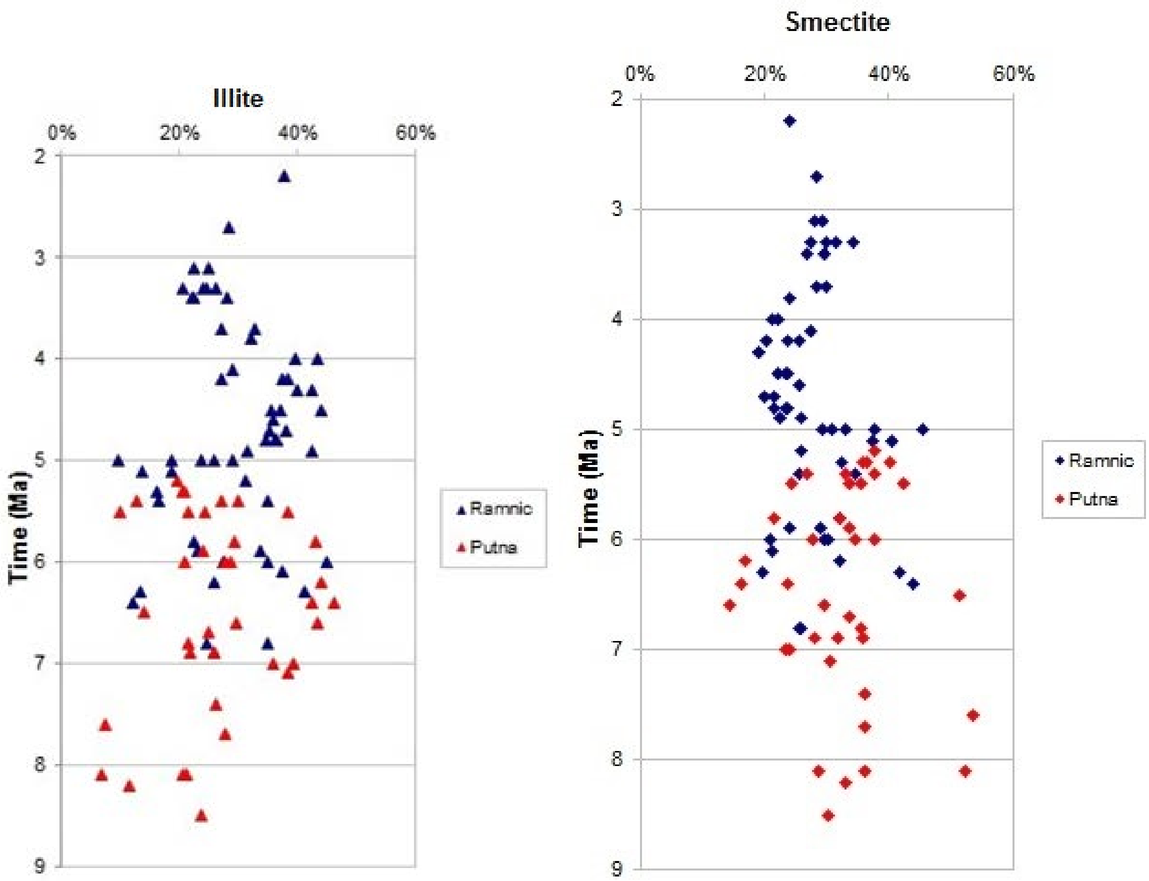

Figure 6. The illite and smectite variation in the cumulated Putna - Râmnicu Sărat sequence referred as Ma (red dots – Purna series, dark-blue dots – Râmnicu Sărat section).

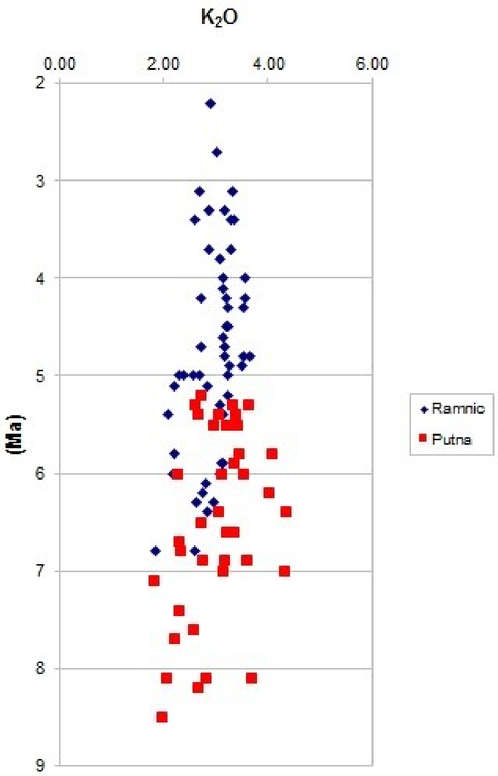

Figure 6. The K_2O availability in the system. (the cumulated Putna - Râmnicu Sărat sequence referred as **Ma** (red dots – Putna series, dark-blue dots – Râmnicu Sărat section).

Plates, during the Jurassic-Tertiary period, produced a series of subduction zones and collision belts (Schmid et al., 2008; Handy et al., 2010). The Focsani Basin is located in the south-eastern Carpathian arch, characterized by the occurrence of medium-scale earthquakes, with epicenters that are placed in a narrow, almost vertical plan (Roman, 1970; Fuchs et al., 1979; Oncescu et al., 1984; Wenzel et al., 1998). Older studies (McKenzie, 1970, Fuchs et al.,1979) attribute the origin of epicenters to the lithosphere diving in the mantle, in an almost vertical direction.

Based on tomographic studies, Wortel & Spakman (2000) and Sperner & Lillie (2001) proposed a model comprising the subduction of an ocean plate under the Oriental Carpathians, followed by a detachment of a "slab" that migrated in the last 10 Ma. In this model, the seismogenesis in the Vrancea region (the Focsani Basin) corresponds to the final detachment phase of the lithospheric slab and explains the temporal progression of Neogene volcanism in the Eastern Carpathians (Seghedi et al., 2004). On the other hand, Knapp et al., (2005) proposes an alternative model for seismicity in the Vrancea area: the delamination of the continental lithosphere, due to the closure of an intracontinental basin in Miocene, accompanied by the thickening of the lithosphere.

Regardless of the proposed tectogenetic model, subduction and detachment of a lithospheric slab or lithosphere delamination, the foreland area from the Carpathian curvature presents a gravitational instability, highlighted by the current position of the Tertiary deposits and confirmed by the mineralogical association in the clay fraction. The deformation of this foredeep basin started in Pliocene, resulting in a near vertical tilting and erosion on the western flank (Dumitrescu & Săndulescu 1970; Tărapoancă et al., 2003). In other words, the smectite-illite transition did not take place because the deposits were never buried at the depth suggested by their thickness but, due to the gravitational rebalancing of the lithosphere, they were pushed away to the East during deposition avoiding the stability field in which the transformation would have been possible.

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REFERENCES

Boles, J.R. & Franks, S.G., 1979. *Clay diagenesis in Wilcox sandstones of Southwest Texas: Implications of smectitediagenesis on sandstone cementation*, J. Sedim. Petrol. 49, 55-70.

Burst, J.F., 1959. *Postdiagenetic clay mineral environmental relationships in the Gulf Coast Eocene*, C & CM 6th Nat. Conf. 1957, pp. 327-341.

Burst, J.F., 1969. *Diagenesis of Gulf Coast clayey sediments and its possible relation to petroleum migration*, Amencan Association of Pelroleum Geologists Bulletin, 53. 73-93.

Dumitrescu, I. & Sandulescu, M., 1970. *Tectonic Map of Romania, Scale 1:1.000.000. Geological Atlas*, sheet no. 6, Inst. Geol. Rom., Romania

Fuchs, K., Bonjer, K.-P., Bock, G., Cornea, I., Radu, C., Enescu, D., Jianu, D., Nourescu, A., Merkler, G., & Tudorache, G., 1979. *The Romanian earthquake of March 4, 1977; II, Aftershocks and migration of seismic activity*. Tectonophysics, 53, 225±247.

Grasu, C., Catana, C. & Bobos, I., 1999. Molasa Carpatilor Orientali. Petrografie si sedimentogeneza, 227pp, *Ed. Tehnica*, Bucharest (Romania).

Handy M.R., Schmid, S. M., Bousquet R., Kissling, E. & Bernoulli D., 2010. Reconciling plate-tectonic reconstructions of Alpine Tethys with the geological–geophysical record of spreading and subduction in the Alps. *Earth-Science Reviews* **102**, 121–158; doi: 10.1016/j.earscirev.2010.06.002.

Hower, J., Eslinger, E.V., Hower, M.E. & Perry, E.A., 1976.

Mechanism of burial metamorphism of argillaceous sediment. 1. Mineralogical and chemical evidence, Geol.Soc.Am.Bull., 87, 725-737.

Huang, W. L., 1992. *Illitic clay formation during experimental diagenesis of arkoses*: in *Origin, Diagenesis, and Petrophysics of Clay Minerals in Sandstones*, D. W. Houseknecht and E. D. Pittman, eds., SEPM. Spec. Publ. 47, 49- 63.

Koster van Groos & Guggenheim, 1989. *Dehydroxylation of a Ca- and Mg exchanged montmorillonile*, Am. Min., 74, 627-636.

Knapp, J. H., Knapp, C. C., Raileanu, V., Matenco, L., Mocanu V. & Dinu C., 2005. *Crustal constraints on the origin of mantle seismicity in the Vrancea Zone, Romania: The case for active continental lithospheric delamination*, Tectonophysics, vol. 410, pp. 311–323.

Kunze, G.W., & DixonJ.B., 1986. *Pretreatment for mineralogical analysis, p. 91-100. In A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods.* 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison WI.

MacEwan D.M.C. & Wilson M.J., 1980. *Interlayer and intercalation complexes of clay minerals. P. 203 in: Crystal Structures of Clay Minerals and their X-ray Identification* (G.W. Brindley & G. Brown, editors). Monograph 5, Mineralogical Society, London.

McKenzie, D.P., 1970. *Plate tectonics of the Mediterranean region.* Nature, 226: 239-243.

Moore D.M. & Reynolds R.C., 1997 *X-ray Diffraction and the Identification and Analysis of Clay Minerals*. Oxford University Press, Oxford-New York.

Nadeau, P.H., Wilson, J., Hardy, W.J. & Tait, J.M., 1984. *Interstratified Clays as Fundamental Particles*, Science, 225, 923-925.

Negreanu S., Barbara S. & Avram S., 2018. *Clay minerals identified in red quaternary deposits, from Valea Anilor area (Mehedinţi county, Romania), using XRD and IR absorption analysis*, Carpathian Journal of Earth and Environmental Sciences, August 2018, Vol. 13, No. 2, p. 447 - 452; DOI: 10.26471/cjees/2018/013/038.

Oncescu, M. C., 1984. *Deep structure of the Vrancea region, Romania, inferred from simultaneous inversion for hypocenters and 3-D velocity structure*, Ann. Geophys., 2, 23–28.

Panaiotu Cristina E., Iuliana Vasiliev, Panaiotu, C.G., Krijgsman, W. & Langereis C.G., 2007. *Provenance analysis as a key to orogenic exhumation: a case study from the East Carpathians (Romania)*, Terra Nova, 2, 120-126.

Perry E.D. & Hower J., 1970. *Burial diagenesis in Gulf Coast pelitic sediments*, Clays & Clay Minerals, 18, 165-177.

Rabenhorst, M.C. & Wilding, L.P., 1984. *Rapid method to obtain carbonate-free residues from limestone and petrocalcic materials*, Soil Science Society of America Journal, vol. 48, issue 1, p. 216.

Reynolds R.C. Jr., & Hower J., 1970. *The nature of interlayering in mixed-layer illite montmorillonite*: Clays and Clay Mmerals, 18, 25-36.

Reynolds, R. C., Jr., 1985. *NEWMOD – a Computer Program for the Calculation of One-Dimensional Diffraction Patterns of Mixed-Layered Clays*: R. C. Reynolds, 8 Brook Rd., Hanover, NH.

Roman, C., 1970. *Seismicity in Romania evidence for the sinking lithosphere*. *Nature* (London), 228: 1176-1178.

Sass B.M., Rosenberg P.E. & Kittrick, J.A., 1987. *The stability of illite/smectite during diagenesis: An experimental study*, Geochimica et Cosmochimica Acta, **51**, 2103-2115.

Schmid, S.M., Bernoulli, D., Fügenschuh, B., Matenco, L., Schefer, S., Schuster, R., Tischler, M. & Ustaszewski, K., 2008. *The Alpine–Carpathian–Dinaridic orogenic system: correlation and evolution of tectonic units.* Swiss Journal of Geosciences 101 (1), 139–183.

Seghedi, I., Szakacs, A., Snelling, N.J. & Pesckay, Z., 2004. Evolution of the Neogene Gurghiu Mountains volcanic range (East Carpatians, Romania) based on K-Ar geochronology., *Geol.Carpath*., 55, 325-332.

Sperner B. & Lillie, R.J., 2001. *Vertical motions related to ocean subduction and continental collision: example from the Eastern Carpathians*. E.U.G., XI Journal of the Conference Abstracts, vol. 6 (1), p. 1433.

Środoń J. & Eberl D.D., 1984. Illite, *In Mineralogical Society of America Reviews in Mineralogy*, 13, 495-539.

Środoń J., 1980. Precise identification of illite/smectite interstratifications by x-ray powder diffraction, Clays and Clay Minerals, 28, No. 6, 401-411.

Środoń J., 1981. *X-ray identification of randomly interstratified illite-smectite in mixtures with discrete illite*, Clay Min., 16, 297-304.

Środoń, J., 1978. *Correlation between coal and clay diagenesis in the Carboniferous of the Upper Silesian coal basin.* In: M.M. Mortland and V.C. Farmer (Eds). Proc. Int. Clay Conf. Oxford. Elsevier, Amsterdam, pp. 251-260.

Środoń, J., 1984. *X-ray identification of illitic materials*: Clays and Clay Min., **32**, 337-49.

Tărapoancă M., Bertotti G., Matenco, L., Dinu, C. & Cloetingh S.A.P.L., 2003. *Architecture of the Focsani depression: a 13 km deep basin in the Carpathians bend zone (Romania)*, Tectonics, 22 (6) 13-1– 13-17.

Vasiliev I., Krijgsman W., Langereis C.G., Panaiotu C.E., Matenco L. & Bertotti G., 2004. *Towards an astrochronological framework for the eastern Paratethys Mio-Pliocene sedimentary sequences of the Focsani basin (Romania):* Earth and Planetary Science Letters, v. 227, p. 231-247.

Velde, B., Suzuki, T., & Nicot, E., 1986. *Pressure-temperature-composition of illite/smectite mixed –layer minerals: Niger Delta mudstones and other examples*: C&CM 34, 435-41.

Weaver, C. E., 1957. *The Clay Petrology of Sediments*, Clays and Clay Minerals, 6, pp. 154-187.

Weaver, C.E., 1959. *The Clay Petrology of Sediments*. Clays Mineral, Proc. Natural Conference, Minerals, 6, 154-187.

Wenzel, F., Achauer, U., Enescu, D., Kissling, E., Russo, R., Mocanu, V., & Musacchio, G., 1998. *Detailed look at final stage of plate break-off is target of study in Romania*, EOS, 79, 48, 589–594.

Wortel, R. & Spakman, W., 2000. *Subduction and slab detachment in the Mediterranean-Carpathian region,* Science, 290, 1910-1917.

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