CHANGES IN FACIES, GEOCHEMISTRY AND CLAY MINERALOGY OF A HEMIPELAGIC SEQUENCE (PLIENSBACHIAN–TOARCIAN, MECSEK MTS., S HUNGARY) – A POSSIBLE PALAEOENVIRONMENTAL INTERPRETATION

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Abstract: The Lower Jurassic hemipelagic sequence of the Mecsek Mountains (S Hungary) is comprised of marls with different carbonate content and contains organic-rich sedimentary rock types. Their sedimentological, geochemical and clay mineralogical properties suggest that circulation pattern of the Tethys and the redox state of the basin could be significantly changed by eustatic and/or climatic factors.

Key words: organic matter, trace elements, stable isotopes, X-ray diffractometry, Jurassic, Mecsek Mountains,

In the eastern part of the Mecsek Mountains (Tisza Megaunit, Southern Hungary) Jurassic formations are widely exposed. The Jurassic sequence from the Middle Sinemurian up to the Upper Bajocian is composed of Allgäu-type ’spotted marl’ with maximum thickness of 1500 metres. The ’spotted marl’ forms couplets of rhythmically alternating massive carbonate-rich and shaley carbonate-poor marls and this monotonous series is interrupted in many horizons by organic-rich rocks. These hemipelagites have not been analysed in detail in sedimentological, geochemical and clay mineralogical point of view, only the basic lithological and palaeontological descriptions and a few organic geochemical examinations have been performed (Hetényi 1966; Dulai et al. 1992), organic-rich and organic-poor marls have not been compared with each others. Relations to tectonic, eustatic, climatic and diagenetic effects, their traces in the sedimentological, chemical and mineralogical compositions of the different rock types have not been examined previously. In this presentation, results of the work performed during the last four years are summarized.

Separated sequences in the eastern part of the Mecsek Mts. were selected and studied in detail to compare the various type of hemipelagites of the ’spotted marl’: 1. Pécsvárad, abandoned quarry (Lower Pliensbachian organic-rich, massive dark grey to black calcareous marl); 2.

Templom Hill (Upper Pliensbachian organic-rich black shale which is alternated by massive and platy ’spotted marl’ and intercalated by various proximal turbidites); 3. Farkas Ravine (the same type organic-poor rocks as in the Sequence 2 but the intercalated turbidites have been developed in more distal facies); 4. Réka Valley (Lower Toarcian laminated black shale).

Bed-by-bed microfacies analysis was made by point counting method to describe textural, structural properties and relative abundance of biogenic constituents of hundreds of thin sectioned samples. 78 selected samples were analysed by X-ray fluorescence analysis after acetic acid digestion to measure major and trace element composition. Linear regression values were calculated to evaluate the concentration data statistically. Enrichment factors of the elements relative to Taylor & McLennan (1985)`s PAAS values were determined. Detrital clastic source of the elements was approached by Al-normalisation.

$^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios of the carbonate of 24 rock samples were analysed by Attila Demény at the Geochemical Research Laboratory of the Hungarian Academy of Sciences, Budapest using a Finnigan-MAT delta S mass spectrometer.

Bitumen and kerogen were isolated from selected organic-rich samples to determine traditional organic geochemical parameters (TOC, HCNS, biomarkers). Measurements of Rock Eval pyrolysis were made by Magdolna Hetényi at the University of Szeged. Clay mineral assemblage of 192 samples was examined by X-ray diffraction method after acetic acid digestion and separation of $<2\mu m$ fraction; composition of the mixed-layer phases was estimated by Środoń (1984)`s method.

In thin section, the Lower Pliensbachian samples are bioclastic packstones dominated by recrystallized sponge spiculae, echinoid fragments and benthic foraminifers with agglutined shells. Calcite-filled molds without any inner structure are abundant. These elements seem to be recrystallized radiolarians and/or calcisphaerae. Thin-shelled bivalves and fragments of brachiopods are minor components. Quartz and muscovite silt grains are characteristic terrigenous constituents.

The samples from the younger formations are different in some point of view: the rocks have more micritic, microsparitic matrix, bioclastic wackestone texture appears frequent. Relative abundance of the radiolarians and filaments increases with decreasing amount of silt-sized terrigenous components, mainly in the carbonate-rich ’spotted marl’ beds. The black shale samples contain abundant amorphous organic matter. Discontinuity surfaces related to submarine erosion or omission were not detected.

According to the microfacies properties the sediments deposited under the storm wave base in a deep shelf margin or in an intrashelf basin. Sedimentation was presumably continuous. Influence of the submarine gravity mass flows cannot be observed in the background sediments. However, nepheloid plume activity could play minor role in forming of the carbonate-rich beds. Terrigenous components are derived from low-rank metamorphic provenance according to the dominance of polycrystalline quartz and white mica over feldspars.

The major element composition of the studied samples can be explained by a simple two-component mixing model with average shale and calcium carbonate as end members. In addition to the two main components, minor biogenic silica are present throughout the succession of the ’spotted marl’. Terrigenous silica as diluting factor plays important role mainly in the Lower Pliensbachian massive marls. Major element composition of the black shale does not differ from the average shale.

On a carbonate-free basis, the concentrations of most the trace elements do not exhibit significant deviations from the average shale. Most of the redox sensitive trace elements (Co, Cr, Cu, Mo, Ni, Pb, V, Zn) seems to have been adsorbed onto the clay minerals supported by the clear significant correlation with the detrital components (Al, Ti, Nb, Y, Zr). The Lower Toarcian black shale is enriched in most of the trace elements relative to the average shale. This phenomenon could be caused by significant biogenic and/or redox-controlled trace element fixation from the seawater.

The organic-rich sediments of the sequences were studied in detail concerning the redox state during and after deposition using S-TOC-Fe relationship. The Lower Pliensbachian rocks (together with the normal massive ’spotted marl’ samples measured as control) scatter near the value of S/TOC = 0.4 that is characteristic to the normal marine environments (Berner 1984). In contrast of them, the Upper Pliensbachian and the Lower Toarcian black shales show different pattern. They have relatively low concentrations of reactive iron, therefore pyritisation could not be limited by the metabolisable organic matter but by pore water sulfate or available iron which suggest temporarily increased bioproductivity and/or decreased oxygenation on the seafloor.

Carbonate stable isotopic composition of the examined samples suggests a significant diagenetic homogenisation effect. Very low $\delta^{18}O$ values (between –8 and –3) show increased temperature during crystallisation of the carbonate cement. The $\delta^{13}C$ data suggest that considerable amount of the carbonate could be derived from diagenetic decay of the organic matter. (Demény, pers. comm.).

Organic geochemical examinations were made on the extracted bitumen and on the kerogen. Dominance of the relative mature organic matter in the Lower Pliensbachian samples is supported by the pristane/phytane ratios (Pr/Ph>1) and by the peaks at C_{15}-C_{20} range with a near harmonic decrease in n-alkane abundance with increasing carbon number. Properties of the extracts from the Upper Pliensbachian samples can be consistent with the relative high abundance of terrigenous organic matter shown by richness of long-chain alkanes and the presence of highly oxidised, probably redeposited terrigenous organic matter.

The m/z 191 and m/z 217 mass fragmentograms display a wide range of biomarkers. Presence of oleanane, lupane, stigmastane and C_{28}-C_{29} dominance of sterane distribution indicate mixed origin of the organic matter of all the samples. Higher abundance of friedelane and gammacerane in the Lower Pliensbachian and Lower Toarcian rocks suggest higher amount of marine organic matter in extracts of these samples relative to the Upper Pliensbachian rocks. Increasing Ts/Ts+Tm ratio, increasing %20S(C_{29}) values, decreasing amount of diasteranes show an upsection decreasing thermal maturity.

The samples can be divided into three populations according to their Rock-Eval parameters. As far as thermal maturity is concerned the Lower Pliensbachian samples are in the oil window and the Upper Pliensbachian rocks are nearby the lower boundary of the oil zone. The Lower Toarcian black shales are immature. All the examined samples have type II kerogen. The Pliensbachian samples show affinity to the type III kerogen (Hetényi, pers. comm.).

According to the TOC and elemental analysis the Lower Toarcian samples have high TOC values and they are rich in nitrogen. Pliensbachian rocks are poor in TOC relative to the Lower Toarcian black shales and they form two groups according to their C/N ratios. The Upper Pliensbachian marls are characterised by N-poor organic matter but the organic matter of the Lower Pliensbachian massive marls have higher C/N ratio than do those of the Upper Pliensbachian marls.

Our data show different maturity of the examined samples in accordance with their stratigraphic positions and burial history. High degree of thermal maturity of the Lower Pliensbachian rocks suggests that their HI values could have been progressively reduced relative to the 'original' (before burial) therefore affinity to the type III kerogen seems not to be so significant as in the case of the Upper Pliensbachian rocks. Our data suggest mixed origin of organic matter of all measured samples. Role of terrigenous organic matter seems to be the most important in the case of the Upper Pliensbachian marls. Nitrogen-rich organic matter is a significant constituent of the Lower Toarcian black shales and in smaller degree of the Lower Pliensbachian massive calcareous marls.

Clay mineralogical composition of the examined Pliensbachian sedimentary rocks is characterised by the dominance of illite, illite/smectite mixed-layer minerals and kaolinite. Mixed-layer illite/smectite minerals could have been carried from pedologic blankets of a relatively distant source area by aeolian transport. Their illite proportion suggests up to 130°C diagenetic heating. Contrasting, the Lower Toarcian black shales have very high amounts of kaolinite relative to the Pliensbachian sediments and the illite proportion of their illite/smectite mixed-layer minerals indicates ~ 100°C heating during diagenesis. These observations could indicate increased humidity and /or dramatic changes in the circulation pattern of the Tethys during the Lower Toarcian.

The sedimentological, geochemical and mineralogical properties of the rocks seem to be correlate with the eustatic and climatic history of the Tethys. According to the Haq et al. (1987) and Hallam (2001) the Late Pliensbachian is characterised by a significant regressive trend. This scenario could be favourable for the intensive turbidite activity, rapid burial of mainly terrigenous organic matter as a result of increased sedimentation rate triggered by lowstand progradation. During the Pliensbachian the deposited sediments could be oxidised that could prevent redox-controlled enrichment of the trace element. High productivity, deposition of significant amount of marine organic matter, temporarily anoxic seafloor with sluggish circulation could be caused by the Early Toarcian transgression, stabilised estuarine circulation and more humid climate.

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