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ORIGINAL RESEARCH PAPER

Occurrence and significance of smectite in the Pliensbachian (Lower Jurassic) at Lókút (Bakony Mts., Hungary)

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ABSTRACT

Although the Mesozoic rocks of the Transdanubian Range have been the subject of a multitude of different studies, mineralogical research is largely underrepresented. The clay mineralogy of Lower Jurassic (especially the Pliensbachian and Toarcian) strata was broadly investigated earlier; however, systematic high-resolution clay mineralogical studies remain scarce. Here we present a mineralogical study focusing on the Upper Pliensbachian strata of the Lókút-Hosszúárok section, located near the Eplény Manganese Ore Field. We identified dioctahedral smectite, randomly interstratified illite/smectite, illite as 10 Å phyllosilicate, quartz and cristobalite. Based on our new results we propose that the smectite was formed by aging of Mg or Fe hydroxide-silica precipitates. The smectite and cristobalite were presumably formed from the siliceous tests of radiolarians, whose abundance was controlled by a local upwelling system. The occurrence of Pliensbachian smectite in the Lókút outcrop shows similarities with the Úrkút smectites known from both Pliensbachian and Toarcian strata, which implies that similar processes controlled the sedimentation during the Pliensbachian as well as during the black (gray) shale-hosted ore accumulation in the Eplény and Úrkút basins.

KEYWORDS

Toarcian oceanic anoxic event, Transdanubian Range, Lókút, smectite

INTRODUCTION

Jurassic sedimentary strata of the Transdanubian Range are dominated by carbonates and have been the broader focus of scientific research. However, from a mineralogical aspect, beside the carbonate minerals, only a few studies have been devoted to accessory minerals; investigation of clay minerals has been scarce. An exception is the comprehensive study of Viczián (1995) who carried out a large-scale clay mineral investigation in the entire Transdanubian Range but only at a low stratigraphic resolution. In the last decade, Polgári et al. (2013) and Leskó et al. (2019) reported new results from topical investigations in a small area but at high spatial resolution. Clay mineralogy is remarkably suitable for reconstruction of depositional environments, because the formation of the different clay minerals is well-defined, and such information will complement and enhance our previous knowledge from other studies. We conducted a clay mineralogy study at the Lókút-Hosszúárok outcrop ("long trench" near the village of Lókút), a stratigraphic key section in the Bakony Mts. (Konda, 1970), which is located close to the Eplény manganese ore deposit. We investigated the occurrence of clay minerals within the Pliensbachian strata, with a special focus on the occurrence of smectite.

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Previously, smectite was only known to occur in the Lower Jurassic of the Transdanubian Range in the in the Úrkút manganese ore field and within the footwall of this deposit (Viczián 1995; Polgári et al. 2013; Leskó et al. 2019). The other economically significant manganese ore deposit in the Transdanubian Range occurs near Eplény, and previous comparisons of the Úrkút and Eplény deposits assumed similar genetic models. The hypothesis that their formation process was the same implies that the depositional environment and the sedimentary strata should be the same or similar (Konda, 1970; Polgári et al., 2000; Szabó, 2006; Bíró et al., 2012; Horváth et al., 2014; Bíró & Pál-Molnár, 2015; Papp et al., 2015; Papp & Zajzon, 2016; Papp & Zajzon, 2019). To test this, we investigated the occurrence of smectite in the Pliensbachian limestone at the Lókút-Hosszúárok outcrop, because of its proximity to the Eplény manganese deposit.

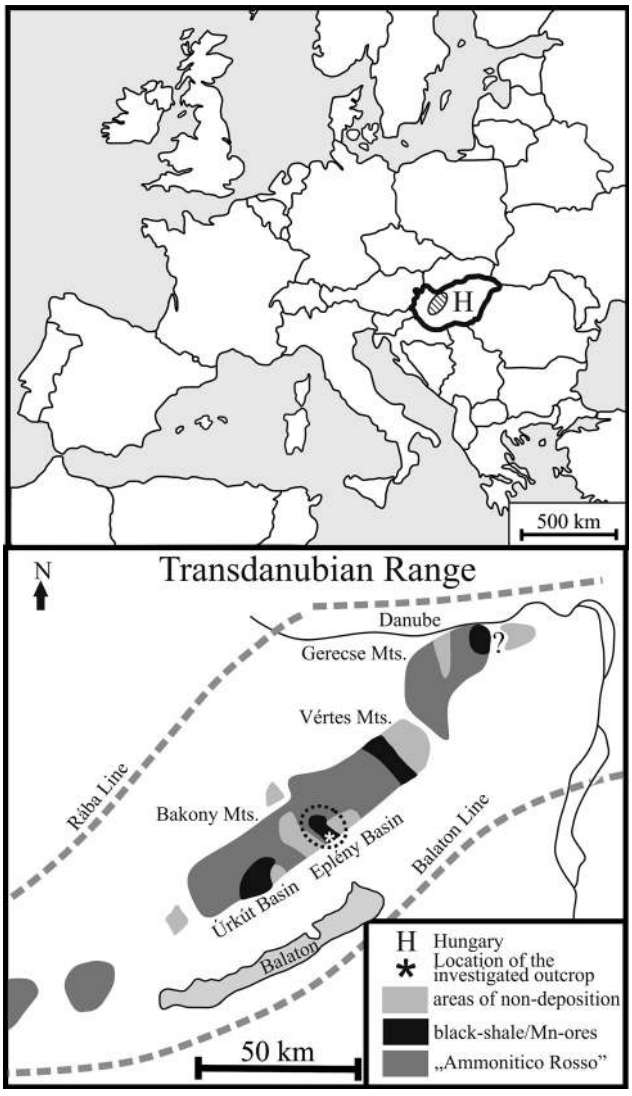

Fig. 1. Location of the studied area in the Eplény Basin, Bakony Mts., within the Transdanubian Range, Hungary (after Vörös & Galácz 1998)

Geologic setting

The study area is located in the Bakony Mts., (Transdanubian Range, TDR), Hungary (Fig. 1). The TDR belongs to the Alps-Carpathians-Pannonian Basin region, to the ALCAPA Mega-unit (Csontos et al., 1992), with an original paleogeographic position reconstructed as between the Upper Austroalpine and the South Alpine lithosphere fragments (Kázmér & Kovács, 1985; Haas et al., 1995, Gawlick et al., 1999; Csontos & Vörös, 2004). The Mesozoic sedimentation in the entire TDR was influenced by the opening of the western part of the Tethys Ocean (Fig. 2). The Mesozoic sedimentary cycle as preserved in the TDR began with a latest Paleozoic transgression. By the end of the Triassic an extensive, coherent, few km-thick Dachstein-type platform developed (Haas, 1988; Haas & Budai, 1995; Haas et al., 1995; Balog et al., 1997; Haas & Budai, 1999; Haas, 2004; Péró & Haas, 2004). The carbonate platform started to disintegrate near the Triassic-Jurassic boundary because of the continuing rifting and spreading of the Neotethys Ocean. In the Early Jurassic the extensive Triassic carbonate platform was fragmented; by the late Early and Middle Jurassic a dissected submarine topography of "seamounts" and

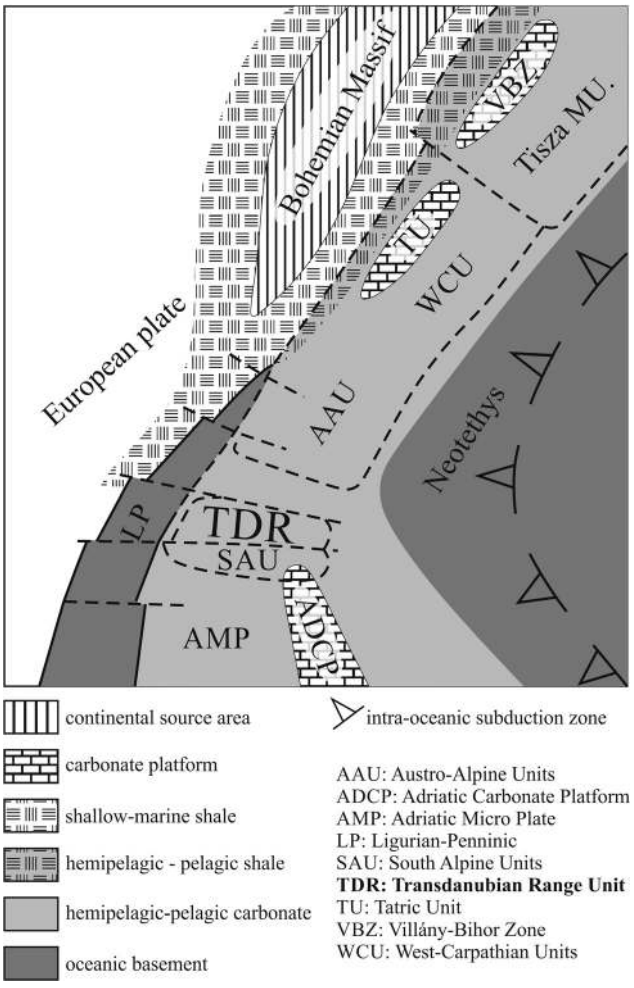

Fig. 2. Paleogeographic position of the Transdanubian Range in the latest Early to early Middle Jurassic (after Haas 2012)

intervening deep basins developed; whereas the Late Jurassic was characterized by a relative shallowing of the pelagic basin (Galácz & Vörös, 1972; Vörös & Galácz, 1998).

During the Jurassic, some parts of the fragmented platform remained in an elevated position ("seamounts"), where condensed red nodular limestone was deposited and hardgrounds were developed. Other blocks subsided and occupied deeper parts of the basin. Sediment was redistributed from the seamounts to the deep basins by bottom currents, resulting in the lack of sedimentation, condensed sections and hardgrounds on the submarine topographic highs. At the bottom of the fault-controlled slopes Hierlatz Limestone, a peculiar brachiopodal–crinoidal limestone facies was developed. Farther from the slope, deep marine sediments were deposited in the basin. In summary, whereas the Triassic is characterized by extensive, widespread and thick shallow marine sedimentary units, in the Jurassic only a relatively thin package of strata was formed (Konda, 1970; Galácz & Vörös, 1972; Galácz et al., 1985; Galácz, 1988; Haas, 1988; Vörös & Galácz, 1998; Haas, 2012).

The Lókút-Hosszúárok outcrop is an artificial trench, excavated in the late 1960s on the Lókúti-domb (Lókút Hill), 1.5 km east-southeast of the village of Lókút (Konda, 1970), which exposes one of the most complete and thickest Lower Jurassic successions of the Bakony Mts. in a local basinal setting. A detailed ammonite biostratigraphy of the fossiliferous strata documented the presence of all three zones of the Lower Pliensbachian in condensed, only a few meter-thick red nodular limestone (*ammonitico rosso*) facies of the Tűzkövesárok Formation (Géczy, 1976), intercalated in the Isztimér Formation (Konda, 1987). The upper part of this latter formation is only 4.5 m thick, and it consists of grey, cherty, sparsely crinoidal limestone and yielded an ammonite fauna that is assigned to the Spinatum Zone of the Upper Pliensbachian (Géczy, 1972). In addition, it also contains a moderately diverse brachiopod assemblage (Vörös, 2009). The base of this unit is an unconformity and the lower part of the Upper Pliensbachian, i.e., the Margaritatus Zone, is missing (Géczy, 1972). This unit is also unconformably overlain by the Toarcian Úrkút Manganese Ore Formation above a manganiferous hardground. Locally, the Úrkút Formation is ~4 m thick, represented here by dark grey and brown pelitic rock and radiolarian-bearing marlstone. Figure 3 illustrates the detailed stratigraphy of the Upper Pliensbachian layers as measured during our sampling.

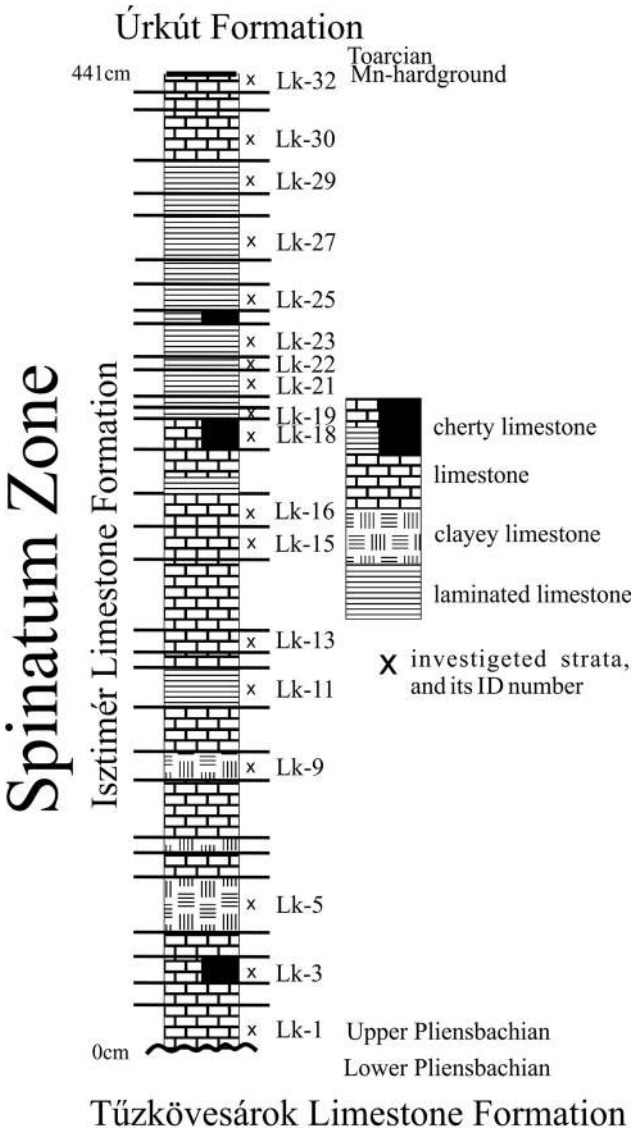

Fig. 3. Schematic section of the sampled Upper Pliensbachian layers of the Lókút-Hosszúárok outcrop

ANALYTICAL METHODS

The analytical work for this project was carried out in the laboratories of the Institute of Mineralogy and Geology at the University of Miskolc. For clay mineralogical studies, a total of 18 carbonate samples collected from the section were dissolved in 5 m/m% acetic acid (CH_3COOH) and then washed with distilled water until they reached the pH of 5–5.5. The samples were dissolved in one piece, without any grinding in order to possess intact insoluble material for further investigations including SEM analysis. The <2 μm grain size fraction was separated by the gravitational method in a distilled water column. The settling time was determined using Stokes' law (Gibbs, 1965). From the settled material, bulk X-ray powder diffraction measurements were made to identify the (060) reflections of the clay minerals for octahedral type assignment. Subsequently, the "pipette-on-glass-slide" method (Brindley, 1961) was used to prepare oriented specimens.

X-ray powder diffraction (XRD) measurements were carried out using a Bruker D8 Advance diffractometer, applying Cu-Kα radiation, 40 mA tube current and 40 kV accelerating voltage, parallel beam geometry obtained with a Göbel mirror in reflection geometry, Vantec-1 position-sensitive detector with 1° detector window opening and 0.007° 2θ/14 s goniometer speed. Instrumental parameters of the oriented clay mineral measurements were the same, the only difference being a longer, 29 sec-counting time. From the residual material the <2 μm grain size fraction was

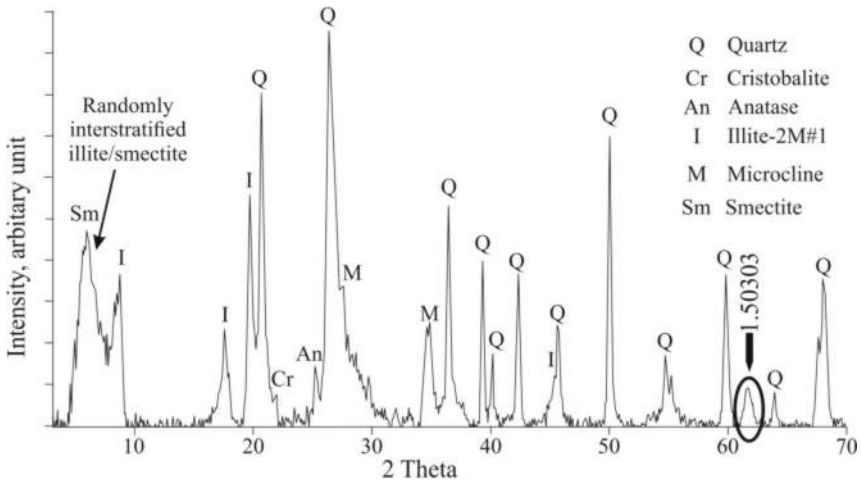

Fig. 4. Representative XRD pattern of the LK-9 sample from the investigated section. The 060 reflection of unoriented clay minerals (grain size >2 μm) is indicated by an ellipse

separated for both random powder and oriented XRD measurements. The random powder measurements allowed identification of the (060) peaks of the clay minerals.

Two oriented specimens were prepared from every sample; first both were measured in air-dry state, after which one was treated with ethylene glycol using the vapor method of Brunton (1955) to determine the swelling. The other sample was measured after heating to 350 and 550 °C, to observe structural collapse.

Identification of crystalline phases was carried out by the Search/Match algorithm in DiffracPlus EVA on the ICDD PDF2 (2005) database. For quantitative mineral composition analysis Rietveld refinement was used, which was performed using TOPAS4 software with empirical instrument parameterization on the NIST SRM640d Si standard; crystal structure data for calculations were obtained from the AMCSD [22] database.

Scanning electron images were taken on the LK-3; LK-13 and LK-18 samples, where a high amount of residual material was observed after the acetic acid leaching, with a ThermoFisher Helios G4 PFIB CXe electron microscope (high voltage 20 keV; beam current 3.2 nA). Chemical analyses were carried out with a Jeol JXA 8600 Superprobe electron microscope (high voltage: 20 keV; beam current 20 nA) on 15 samples.

RESULTS

After the acetic acid treatment of the pinkish gray limestone samples, an increase of the insoluble residue was observed upsection throughout the Upper Pliensbachian (from 0.5 m/m% up to 5–6 m/m%). Some of the samples yielded a high amount of residue (~40–45 m/m%) because of the silicification of the limestone. The silicification of some samples (e.g., Lk-18) was apparent already in the outcrop, whereas for others (e.g., Lk-13) the silicification was only revealed in the laboratory after the acetic acid treatment.

Following Rietveld refinement, the mineralogical composition of the residue shows only limited variation throughout the entire section: the quartz content is 65–71 m/m%, other components include illite (18–22 m/m%), smectite (3–6 m/m%), muscovite (3–4 m/m%), anatase (~0.5 m/m%), and albite (~0.15 m/m%). In some samples there are additional detrital components such as orthoclase (1–2 m/m%) and Mn-oxides (<0.5 m/m%). There are no outstanding high or low abundance values throughout the profile.

During the clay mineral study, the (060) reflections exhibited a peak at 1.503 Å (Fig. 4) which indicates the dioctahedral nature of both smectite and illite. All the oriented clay-mineral samples display peaks at ~15 Å in air-dry state, which is shifted to 17–17.5 Å during glycolation (Fig. 5) and collapsed to ~10 Å after heating. The 15 Å peak is not specific to dioctahedral smectite; rather it is interpreted to result from the exchange of interlayer cations to Ca and its hydration layer, which was caused by the acetic acid leaching (Moore & Reynolds, 1997). Beside smectite, other phases include randomly interstratified illite/smectite, illite, quartz and cristobalite. Table 1 shows representative SEM-EDS results (<2 μm grain size) from the investigated section. The smectite is not characterized in detail (i.e., with regard to cation content) because cation exchange and oxidation of Fe could happen during the acetic acid leaching.

The crystallite size of the illite in the residual material was defined by Rietveld refinement as ~15nm. Cristobalite crystallite size was determined by the same method as ~25 nm. Within the randomly interstratified illite/smectite, a ~70–80% smectite and 20–30% illite proportion was determined after Środoń (1980) and Inoue et al. (1989). This composition is characteristic throughout the entire studied section.

Silicified limestone layers found in the investigated section include LK-3, LK-13 and LK-18. In these silicified strata the quartz content is between 30 and 42 m/m%. According to the SEM observations, most of the SiO_2 content is related to biogenic silica derived from fossils with siliceous skeleton (Fig. 6), although the siliceous microfossils are strongly recrystallized.

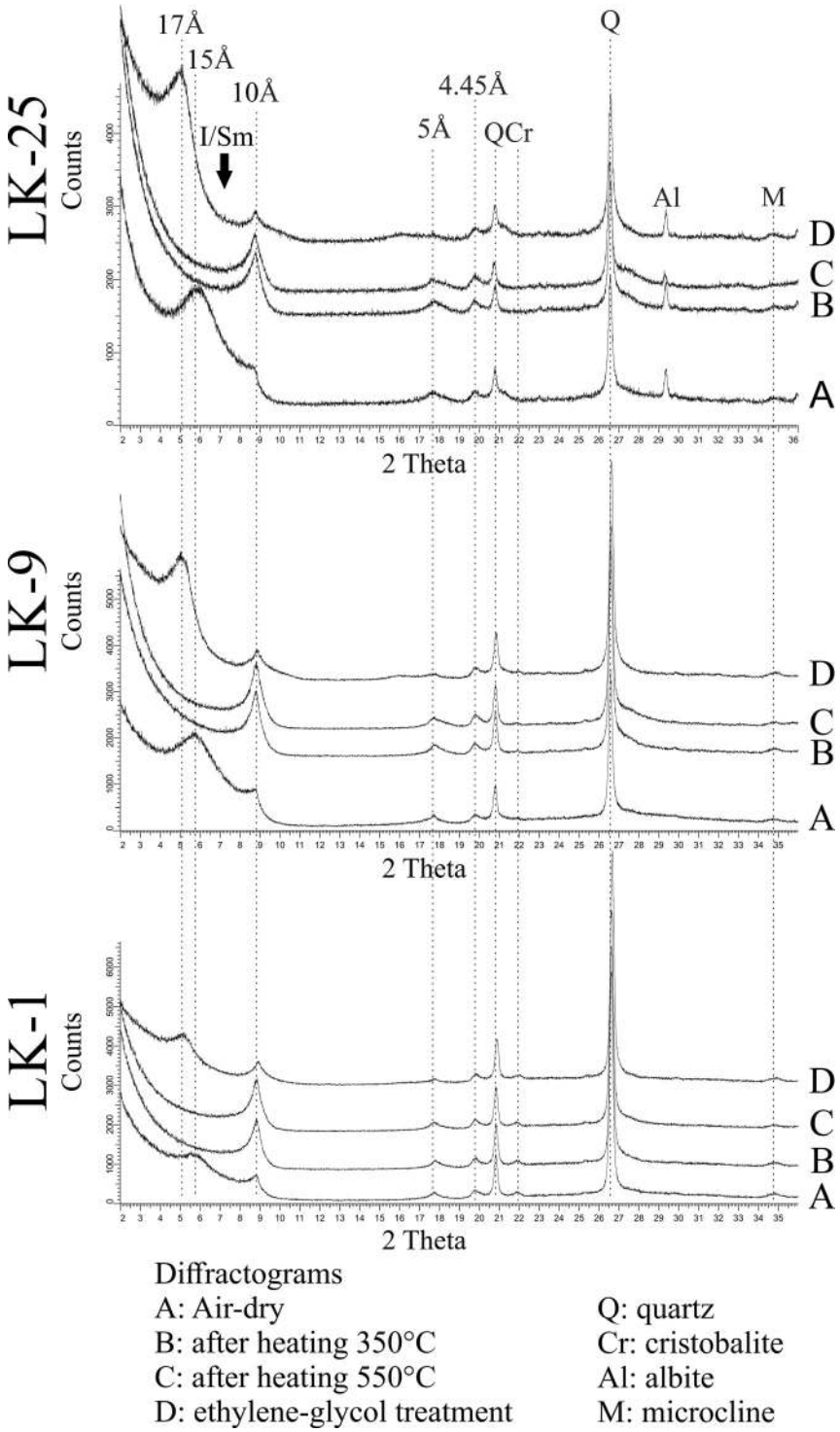

Fig. 5. Representative XRD patterns of the lower, middle and upper part of the Upper Pliensbachian section. Note the smectite peaks shifting from 15 Å to 17–17.5 Å after ethylene-glycol treatment and to 10 Å after heating

DISCUSSION

According to previous studies (Kaeding et al., 1983; Viczián, 1995; Polgári et al., 2013), the smectite content of Lower Jurassic strata in the Transdanubian Range was unique, restricted to the Úrkút Manganese Ore deposit, in the Toarcian black or grey shale and ore bodies. However, Leskó (2014) reported smectite for the first time below the Úrkút manganese ore deposit, from the Pliensbachian footwall. Leskó et al. (2019) proved that smectite is ubiquitous close to the Úrkút Manganese deposit within the Pliensbachian footwall.

Smectite in such facies could form in several different ways; its genesis is most commonly related to various

Table 1. Chemical composition of the dissolution residue from representative samples determined by SEM-EDS. Concentrations are expressed in m/m%

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_3	SO_2	K_2O	CaO	TiO_2	FeO
LK-11	0.66	1.60	7.48	82.67	1.65	0.38	1.44	0.67	0.15	3.30
	0.99	1.78	7.49	82.32	1.55	0.58	1.41	0.66	0.15	3.06
	0.42	1.32	6.84	83.66	1.64	0.40	1.29	0.70	0.16	3.56
LK-23	0.81	2.17	9.57	78.30	1.06	0.46	1.73	0.65	1.37	3.87
	0.50	1.98	9.80	79.86	0.84	0.39	1.69	0.70	0.25	3.98
	1.60	2.78	9.30	78.60	1.19	0.65	1.53	0.49	0.32	3.53
LK-27	0.47	1.88	9.79	79.59	0.66	0.13	1.85	0.56	0.14	4.93
	0.66	2.33	10.36	74.98	1.51	0.48	1.71	0.94	1.60	5.43
	0.48	1.87	9.69	80.18	0.68	0.49	1.50	0.65	0.13	4.33

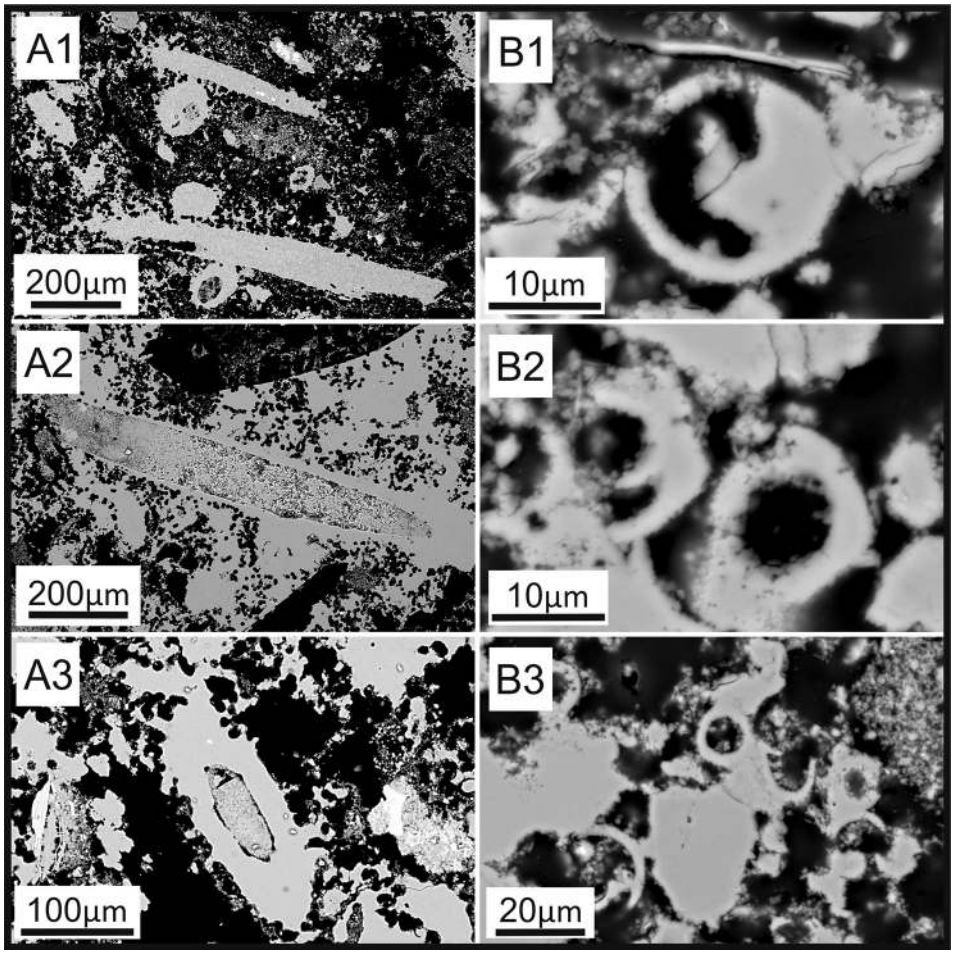

Fig. 6. SEM-BSE images from siliceous skeletons from the investigated section. Images were taken from samples LK-3: A1-B1; LK-15: A2-B2; LK-18: A3-B3

magmatic/volcanic and hydrothermal events or related alteration (Bischoff, 1972; Hein & Scholl, 1978; Seyfried et al., 1978; Cole, 1983; Bustillo & Martínez-Frías, 2003; Lantenois et al., 2008). Smectite could also form at low temperature by aging of hydrated silica colloid in the presence of the required cations, as was proven by laboratory experiments on freshly-prepared hydroxide–silica precipitates by Harder (1972, 1976). A recent research by Schöllhorn et al. (2020) found evidence for Pliensbachian magmatism/volcanism in Switzerland and in England. Mercury content of the investigated rock units could be related to coeval magmatic/volcanic events (Varekamp & Buseck, 1986; Nriagu & Becker, 2003). Schöllhorn et al. (2020) documented that the increase of Hg concentration correlates with increasing phyllosilicate content. Unfortunately, quantitative details of the abundance and ratio of the different types of phyllosilicates are not provided in their study, where the Hg refers to coeval magmatic/volcanic events. According to their study their smectite and illite ratio change was caused by climate changes. There is no evidence

in the entire Transdanubian Range for Pliensbachian igneous rocks, tuffs, volcanic glasses, elevated mercury content, or outstanding peaks of phyllosilicate content; thus, a genetic model that invokes any magmatic or volcanic event could be excluded (Polgári et al., 2013; Leskó et al., 2019). However, the other model is more plausible for the genesis of smectite reported here and is likely to explain the occurrence of smectite in the studied deposits at Lókút-Hosszúárok. This process is also thought to be responsible for the smectite formation in the Úrkút Basin (Polgári et al., 2013; Leskó et al., 2019).

The randomly interstratified illite/smectite is generally formed through illitization of the smectite during the diagenesis. The proportion (~70–80% smectite and 20–30% illite) shows that the illitization progress was at its beginning: the sediment was buried only at shallow depth and the temperature was low (<100 °C) (Jennings & Thompson, 1986; Velde et al., 1986; Środoń, 1999; Bergaya et al., 2006; Caudros, 2006). This result fits with the models of the local (Bakony Mts.) and regional geologic history as well (Konda, 1970; Galácz et al., 1985).

The SEM-EDS results support the XRD results. The SiO_2 content is related to the high amount of quartz and other silicates. Illite and smectite are the main carriers of Al and Mg. Because of the cation exchange of the acetic acid treatment, Ca can occur within the smectite; K and Na relate to illite. Fe is a constituent of smectite and nanocrystalline Fe-oxide; the latter is responsible for the color of the red or pinkish limestones. P and S are likely tied to the Fe-oxides. However, no unambiguous conclusion can be drawn from the SEM-EDS results because we measured bulk composition, since the grain size of the individual crystals is too small. It was not possible to determine the chemical formula of the smectite, because multiple phases were analyzed simultaneously.

The grain size of the illite suggests the extrabasinal (i.e., detrital) origin, and the mineral composition (phyllosilicates, quartz, feldspars) of the residue assumes a sedimentary sea basin environment (Bergaya et al., 2006), which is in agreement with the previous sedimentary models of the TDR.

The silica content of the silicified limestone layers, cristobalite and partly quartz, which was found in the insoluble residue after leaching, is derived from siliceous fossils: sponges and radiolarians (Fig. 6) (Konda, 1970; von der Borsch et al., 1971; von Rad & Rösch, 1972; Cole & Shaw, 1989; Williams & Crerar, 1985; Dixit et al., 2001). Figure 6 shows remains of siliceous sponges (A1 from LK-3; A2 from LK-13 and A3 from LK-18; Moore, 1967; Matranga, 2015), and presumably radiolarian tests (B1 from LK-3; B2 from LK-13 and B3 from LK-18; Anderson, 1983; Baumgartner et al., 2007). All of the siliceous fossils are strongly recrystallized. The large amounts of radiolarians, which could contribute to bulk silicification of certain layers, suggest the presence of a local upwelling system, as upwelling could cause local radiolarian blooms (Smith, 1968; Hartline, 1981; Molina-Cruz, 1984).

Considerable similarities exist between the Eplény Basin and the Úrkút Basin, including the economically significant accumulation of black shale-hosted manganese ore, which is restricted to these two occurrences in the Transdanubian Range, and the asymmetric geometry of sedimentation patterns (i.e., similar trends of sedimentation on opposite sides of seamounts and intervening basins; Vörös & Galácz, 1998). In addition, the large amount of biogenic silica, likely derived from radiolarians, is also comparable in the Pliensbachian strata in both basins, in Úrkút in the form of the peculiar lithology referred to as "tripoli" (Polgári et al., 2005; Leskó et al., 2019) and in Lókút represented by cristobalite and silicified carbonate layers. Localized upwelling systems can account for these observations, similar to the paleogeographic-paleoceanographic model developed for older, Middle Triassic silica-rich deposits in the Transdanubian Range (Budai et al., 2017).

Smectite was found in the Upper Pliensbachian strata only in the Eplény and Úrkút Basins, where there is an increased siliceous fossil content (radiolarites and spongiolites) (Polgári et al., 2015; Leskó et al., 2019), which could relate to upwelling events. Furthermore, smectite appears where a large amount of manganese relates to the Jenkyns Event. However, smectite was not identified in other parts of the Transdanubian Range; although other evidence of the Jenkyns Event can be encountered, there is no evidences of elevated siliceous bioaccumulation in the Upper Pliensbachian record, and no significant manganese accumulation in the Toarcian rocks. The Upper Pliensbachian layers do not have any smectite content in the Tölgyhát Quarry, Gerecse Mts., (Leskó & Zajzon, 2015; Leskó et al., 2015), which widely studied location represents the Jurassic sedimentation. These results indicate that the smectite appearance relates to the manganese accumulation. This relation was mentioned in former studies (Kaedin et al., 1983; Viczián, 1995) as well, but the present study and Leskó et al. (2019) show that the smectite appearance is more widespread than previous studies indicated; also, the formation of the smectites was interpreted in a different fashion.

CONCLUSIONS

The occurrence of smectite in the Lower Jurassic of the Transdanubian Range is not as restricted as previous studies suggested, as it is not confined to the ore bodies of the Úrkút Manganese Ore Formation but also appears in stratigraphically lower units near the thick manganese-rich deposits within the Transdanubian Range. Our new mineralogical results indicate the presence of dioctahedral smectite and increased quartz and cristobalite content from the Pliensbachian sediments of the Lókút-Hosszúárok outcrop, in agreement with a model that emphasizes analogues with the Úrkút Basin on the basis of similar data. Our study strengthens the arguments that the Eplény and Úrkút Basins were analogous areas with similar paleogeographic position and sedimentary environments during the Early Jurassic, and similarly characteristic mineralogical paragenesis, which could have resulted from the same processes and be explained by congruent genetic

models. Our results are in agreement with other local and regional geologic observations which help to better understand the geologic evolution of the Transdanubian Range.

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REFERENCES

Anderson, O.R. (1983). *Radiolaria*. Springer-Verlag, p. 355.

Balog, A., Haas, J., Read, J.F., and Coruh, C. (1997). Shallow marine record of orbitally forced cyclicity in a Late Triassic carbonate platform, Hungary. *Journal of Sedimentary Research*, 67: 661–675.

Baumgartner, P.O., Aitchison, J.C., Wever, P.D., and Jackett, S-J. (2007). *Radiolaria: siliceous plankton through time*. Birkhäuser, p. 139.

Bergaya, F., Theng, B.K.G., and Lalaly, G. (2006). *Handbook of clay science*. Elsevier, p. 1125.

Bischoff, J.L. (1972). A ferroan nontronite from the Red Sea geothermal system. *Clays and Clay Minerals*, 20: 217–223.

Bíró, L. and Pál-Molnár, E. (2015). Trace and rare earth element geochemistry of the primary manganese ore from Bakony (Hungary). *Bulletin of the Hungarian Geological Society*, 145: 119–126. [in Hungarian].

Bíró, L., Polgári, M., and Pál-Molnár, E. (2012). The revaluation of the drillings of the manganese mineralization in Eplény (Hungary). *Carpathian Journal of Earth and Environmental Sciences*, 7: 109–117.

Brindley, G.W. (1961). X-ray identification and crystal Structure of clay minerals. *Mineralogical Society of London*, 544.

Brunton, G (1955). Vapour pressure glycolation of oriented clay minerals. *American Mineralogist*, 40: 124–126.

Budai, T., Haas, J., Vörös, A., and Molnár, Zs. (2017). Influence of upwelling on the sedimentation and biota of the segmented margin of the Western Neotethys: a case study from the Middle Triassic of the Balaton Highland (Hungary). *Facies*, 63: 22–39.

Bustillo, M.A. and Martínez-Frias, J. (2003). Green opals in hydrothermalized basalts (Tenerife Island, Spain): alteration and aging of silica pseudoglass. *Journal of Non-Crystalline Solids*, 323: 27–33.

Caudros, J (2006). Modeling of smectite illitization in burial diagenesis environments. *Geochimica et Cosmochimica Acta*, 70: 4181–4195.

Cole, T.G. (1983). Oxygen isotope geothermometry and origin of smectites in the Atlantis II deep, red sea. *Earth and Planetary Science Letters*, 66: 166–176.

Cole, T.G. and Shaw, H.F. (1989). The nature and origin of authigenic smectites in some recent marine sediments. *Clay Minerals*, 18: 239–252.

Csontos, L., Nagymarosy, A., Horváth, F., and Kovac, M. (1992). Tertiary evolution of the Intra-Carpathian area: a model. *Tectonophysics*, 208: 221–241.

Csontos, L. and Vörös, A. (2004). Mesozoic plate tectonic reconstruction of the Carpathian region. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 210: 1–56.

Dixit, S., van Cappellen, P., and van Bennekom, A.J. (2001). Processes controlling solubility of biogenic silica and pore water build-up of silicic acid in marine sediments. *Marine Chemistry*, 73: 333–352.

Galácz, A. (1988). Tectonically controlled sedimentation in the Jurassic of the Bakony Mountains (Transdanubian Central Range, Hungary). *Acta Geologica Hungarica*, 31: 313–328.

Galácz, A., Horváth, F., and Vörös, A. (1985). Sedimentary and structural evolution of the Bakony Mountains (Transdanubian Central Range, Hungary): paleogeographic implications. *Acta Geologica Hungarica*, 28: 122–135.

Galácz, A. and Vörös, A. (1972). A bakony-hegységi jura fejlődéstörténeti vázlata a főbb üledékföldtani jelenségek kiértekelése alapján. *Bulletin of Hungarian Geological Society*, 102: 122–135.

Gawlick, H.J., Frisch, W., Vecsei, A., Steiger, T., and Böhm, F. (1999). The change from rifting to thrusting in the Northern Calcareous Alps as recorded in Jurassic sediments. *Geologische Rundschau*, 87: 644–657.

Géczy, B. (1972). Ammonite faunae from the lower Jurassic standard profile at Lókút, Bakony Mountains, Hungary. *Annales Universitatis Scientiarum Budapestinensis de Rolando Eötvös nominatae, Sectio Geologica*, 15: 47–76.

Géczy, B. (1976). *Les ammonitines du Carixien de la Montagne du Bakony*. Akadémiai Kiadó, Budapest, pp. 223.

Gibbs, R.J. (1965). Error due to segregation in quantitative clay mineral X-ray diffraction mounting techniques. *The American Mineralogists*, 50: 741–751.

Haas, J. (1988). Upper Triassic carbonate platform evolution in the Transdanubian Mid-Mountains. *Acta Geologica Hungarica*, 31: 299–312.

Haas, J. (2004). *Geology of Hungary: Triassic*. ELTE Eötvös Press, p. 384.

Haas, J. (2012). Influence of global, regional, and local factors on the genesis of the Jurassic manganese ore formation in the Transdanubian Range, Hungary. *Ore Geology Reviews*, 47: 77–86.

Haas, J. and Budai, T. (1995). Upper Permian–Triassic facies zones in the Transdanubian Range. *Rivista Italiana di Paleontologia e Stratigrafia*, 101: 249–266.

Haas, J. and Budai, T. (1999). Triassic sequence stratigraphy of the Transdanubian Range, Hungary. *Geologica Carpathica*, 50: 459–475.

Haas, J., Kovács, S., Krystyn, L., and Lein, R. (1995). Significance of Late Permian-Triassic facies zones in terrane reconstructions in the Alpine-North Pannonian domain. *Tectonophysics*, 242: 19–40.

Harder, H (1972). The role of magnesium in the formation of smectite minerals. *Chemical Geology*, 10: 31–39.

Harder, H (1976). Nontronite synthesis at low temperatures. *Chemical Geology*, 18: 169–180.

Hartline, B.K. (1981). Coastal upwelling: physical factors feed fish. *Science*, 208: 38–40.

Hein, J.R. and Scholl, D.W. (1978). Diagenesis and distribution of late Cenozoic volcanic sediment in the southern Bering Sea. *Geological Society of America Bulletin*, 89: 197–210.

Horváth, A., Zajzon, N., and Vigh, T. (2014). The distribution of REE in the Úrkút Manganese Formation. In: Szakáll, S (Ed.), *Critical monography series 5*. University of Miskolc, Miskolc, pp. 109–130. [in Hungarian].

Inoue, A., Bouchet, A., Velde, B., and Meunier, A. (1989). Convenient technique for estimating smectite layer percentage in randomly interstratified illite/smectite minerals. *Clays and Clay Minerals*, 37: 227–234.

Jennings, S. and Thompson, G.R. (1986). Diagenesis of Plio-Pleistocene sediments of the Colorado river delta, Southern California. *Journal of Sedimentary Research*, 56: 89–98.

Kaeding, L., Brockamp, O., and Harder, H. (1983). Submarin-hydrothermale Entstehung der sedimantären Mangan Lagerstätte Úrkút/Ungarn. *Chemical Geology*, 40: 251–268.

Kázmér, M. and Kovács, S. (1985). Permian-Paleogene paleogeography along the eastern part of the Insubric-Periadriadriatic lineament system: evidence for continental escape of the Bakony-Drauzug Unit. *Acta Geologica Hungarica*, 28: 71–84.

Konda, J. (1970). A Bakony hegységi júra időszaki képződmények üledékföldtani vizsgálata. (Lithologische und Fazies-Untersuchung der Jura-Ablagerungen des Bakony-Gebirges). *Annual Report of the Geological Institute of Hungary*, 50: 161–260.

Konda, J. (1987). Bakony, Lókút, Lókúti-domb (Lókút Hill, Lókút, Bakony mountains). *Magyarország geológiai alapszelvényei (Geological Key Sections of Hungary). Magyar Állami Földtani Intézet (Hungarian Geological Institute)*, 10.

Lantenois, S., Champallier, R., Bény, J.-M., and Muller, F. (2008). Hydrothermal synthesis and characterization of dioctahedral smectites: a montmorillonites series. *Applied Clay Science*, 38: 165–178.

Leskó, M.Zs. (2014). *Ásványtani vizsgálatok az úrkúti mangánérc karbonátos és oxidos átmeneti zónájának feküjén*, MSc thesis, Eötvös Loránd University, Department of Mineralogy, pp. 81, Manuscript.

Leskó, M.Zs., Papp, R.Z., Topa, B.A., Kristály, F., Vigh, T., and Zajzon, N. (2019). Smectite appearance in the footwall of the Úrkút manganese ore deposit, Bakony Mts., Hungary. *Central European Geology*, 62(1): 100–118.

Leskó, M.Zs. and Zajzon, N. (2015). Nagy felbontású ásványtani vizsgálat a gerecsei Tölgyháti-kőfejtőben. *Tavaszi Szél absztrakt kötet*, 2015: 134.

Leskó, M.Zs., Zajzon, N., Kristály, F., Pálfy, J., and Price, G.D. (2015). Correlation between Toarcian (Early Jurassic) manganiferous sediments from the Tölgyhát Quarry (Gerecse Mts., Hungary) and Úrkút manganese ore deposit (Bakony Mts., Hungary): a mineralogical study. *Acta Mineralogica-Petrographica, Abstract Series*, 9: 38.

Matranga, V (2015). *Echinodermata*. Springer-Verlag, p. 276.

Molina-Cruz, A. (1984). Radiolaria as indicators of upwelling processes: the Peruvian connection. *Marine Micropaleontology*, 9: 53–75.

Moore, R.C. (1967). *Treatise on invertebrate Paleontology: Part S Echinodermata 1*. The Geological Society of America, p. 296.

Moore, D.M. and Reynolds, R.C. Jr. (1997). *X-ray diffraction and the identification and analysis of clay minerals*, 2nd ed. Oxford University Press, Oxford, New York, p. 378.

Nriagu, J. and Becker, C. (2003). Volcanic emissions of mercury to the atmosphere: global and regional inventories. *Science of The Total Environment*, 304: 3–12.

Papp, R.Z., Topa, B.A., Vigh, T., and Zajzon, N. (2015). Geochemical and mineralogical study of Eplény Mn-deposit, Hungary. In: *Goldschmidt 2015 25th anniversary abstracts*, pp. 2399–2399.

Papp, R.Z. and Zajzon, N. (2016). New mineralogical and geochemical results in the research of the Eplény manganese deposit. In: Vanek, F. (Ed.), *18th mining, metallurgy and Geology conference*, pp. 161–165. [in Hungarian].

Papp, R.Z. and Zajzon, N. (2019). Mineralogical study of the abandoned Eplény Mn-ore deposit, Hungary. In: Szabó, N.P., and Papp, R.Z. (Eds.), *Doktoranduszok Fóruma: Miskolc, 2018*. November 22, 28. Műszaki Földtudományi Kar szekciókiadványa, pp. 59–81.

Péró, Cs. and Haas, J. (2004). Mesozoic evolution of the Tisza Mega-unit. *International Journal of Earth Sciences*, 93: 297–313.

Polgári, M., Hein, J.R., Németh, T., Pál-Molnár, E., and Vigh, T. (2013). Celadonite and smectite formation in the Úrkút Mn-carbonate ore deposit (Hungary). *Sedimentary Geology*, 294: 157–163.

Polgári, M., Szabó, Z., Szabó-Drubina, M., Hein, J.R., and Yeh, H.-W. (2005). A porous silica rock ("tripoli") in the footwall of the Jurassic Úrkút manganese deposit, Hungary: composition, and origin through carbonate dissolution. *Sedimentary Geology*, 177: 87–96.

Polgári, M., Szabó, Z., and Szederkényi, T. (2000). *Manganese ores in Hungary*. MTA Szegedi Akadémiai Bizottsága, Szeged, p. 675. [in Hungarian].

Schöllhorn, I., Adatte, T., Charbonnier, G., Mattioli, E., Spangenberg, J.E., and Föllmi, K.B. (2020). Pliensbachian environmental perturbations and their potential link with volcanic activity. Swiss and British geochemical records. *Sedimentary Geology*, 406, https://doi.org/10.1016/j.sedgeo.2020.105665.

Seyfried, W.E.J., Shanks, W.C.I., and Dibble, W.E.J. (1978). Clay mineral information in DSDP leg 34 basalt. *Earth and planetary Science Letters*, 34: 265–276.

Smith, R.L. (1968). Upwelling. *Oceanography and Marine Biology Annual Review*, 6: 11–46.

Środoń, J. (1980). Precise identification of illite/smectite interstratification by X-Ray powder diffraction. *Clays and Clay Minerals*, 28: 401–411.

Środoń, J. (1999). Use of clay minerals in reconstructing geological processes: recent advances and some perspectives. *Clay Minerals*, 34: 27–37.

Szabó, Z (2006). *Mining of the manganese ore, Bakony Mountains*. Manganese Mining and Processing Ltd, p. 655. [in Hungarian].

Varekamp, J.C. and Buseck, P.R. (1986). Global mercury flux from volcanic and geothermal sources. *Applied Geochemistry*, 1: 65–73.

Viczián, I. (1995). Clay mineralogy of Jurassic carbonate rocks, central Transdanubia, Hungary. *Acta Geologica Hungarica*, 38: 251–268.

Velde, B., Suzuki, T., and Nicot, E. (1986). Pressure-temperature-composition of illite/smectie mixed-layer minerals: Niger delta

mudstunes and other examples. *Clays and Clay Minerals*, 34: 435–441.

Von der Borsch, C.C., Galehaouse, J., and Nesteroff, W.D. (1971). Silicified limestone-chert sequences cored during leg 8 of the deep sea drilling project: a petrologic study. In: Tracey, Jr, J.L., Sutton, G.H., (Eds.), *1971 Initial reports of the deep sea drilling project*, Vol. VIII. U.S. Government Printing Office, Washington, pp. 819–827.

von Rad, U. and Rösch, H. (1972). Mineralogy and origin of clay minerals, silica and authigenic silicates in Leg 14 sediments. In: *Initial reports of the deep sea drilling project*, Vol. XIV, pp. 727–751.

Vörös, A. (2009). The Pliensbachian brachiopods of the Bakony mountains (Hungary). *Geologica Hungarica, Series Palaeontologica*, 58: 295.

Vörös, A. and Galácz, A. (1998). Jurassic palaeogeography of the Transdanubian Central Range (Hungary). *Rivista Italiana di Paleontologia e Stratigrafia*, 104: 69–84.

Williams, L.A. and Crerar, D.A. (1985). Silica diagenesis II. General mechanisms. *Journal of Sedimentary Research*, 55: 312–321.