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Silurian volcanism recorded in sedimentary sections at the southwestern margin of the East European Platform: geochemical correlation and tectono-magmatic interpretation

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X-ray fluorescence analyses of sixty-one K-bentonite samples from the Ludlow-Pridoli sections of western Ukraine and Moldova were used for correlation and source magma interpretation. The study reveals that source magmas of K-bentonites were low-temperature (~720°C) rhyolites indicating melting of continental crust during subduction of a hydrated oceanic plate. Volcanic sources were probably located within the developing Scythian Platform embracing the southeastern margin of the East European Platform. The present study demonstrates the potential of using immobile elements for correlating volcanic ash layers between different sections.

Key words: Silurian volcanism, K-bentonites, Ukraine, Moldova, Scythian Platform.

INTRODUCTION

Volcanic ashes generated by eruptions in tectonically active areas frequently reach calm sedimentation areas on stable platforms. These ashes form thin K-bentonite interbeds in sedimentary sections, offering an opportunity for isotopic dating of biostratigraphically well-characterized sections (Bergström et al., 2008; Cramer et al., 2012, 2015), precise correlations (Kiipli et al., 2010), tectono-magmatic interpretation of volcanic processes in source areas (Huff et al., 2000; Hannon and Huff, 2019; Kiipli et al., 2020), deciphering of diagenetic history of basins (Środon et al., 2009) and facies analyses (Hong et al., 2019).

Volcanic ash beds from the southwestern margin of the East European Platform were previously studied by Tsegelnyuk et al. (1983) who identified their stratigraphic position and assigned stratigraphic indices. The clay mineralogy of the Podillyan K-bentonites was studied by Huff et al. (2000). Geochemical data were published by Huff et al. (2000) (5 samples), Kiipli et al. (2000b) (16 samples) and Kaljo et al. (2014) (8 samples). In the present study we have analysed an additional 32 K-bentonite samples using XRF. New materials, with the incorporation of data from previous papers, illustrate the potential of K-bentonites for geochemical correlation of sections. Moreover, the article offers a new interpretation of tectono-magmatic processes at the margins of the Baltica palaeocontinent using new analytical information.

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GEOLOGICAL BACKGROUND

K-bentonites were deposited in the Silurian shelf at the southwestern margin of the Baltica palaeocontinent adjacent to the Paleozoic Rheic Ocean, now belonging to the Podillya and Volyn regions (Ukraine) and Moldova (Fig. 1). Silurian sections, represented by shallow water limestones, dolomites and marlstones, are exposed along the Dniester River banks in the Podillya region (Tsegelnyuk, 1980a, b; Tsegelnyuk et al., 1983; Łuczyński et al., 2016). The thickness of the Silurian section in these exposures, from Telychian to Pridoli, exceeds 300 m. In the Korneshty-2m core from Moldova, the thickness of the Silurian section is 297 m, with gypsum as well as limestones and dolomites occurring in the Upper Ludlow, indicating an arid climate (Kiipli et al., 2000b). Gypsum has also been recorded in borehole cores drilled in the northerly Volyn region (Kaljo et al., 2014). Radkovets (2015) described lagoonal, reef and open shelf facies extending from east to west. The thickness of open shelf facies increases quickly towards the west reaching 1400 m. Open shelf facies in borehole cores are represented by marlstones, argillaceous limestones and shales that frequently contain some organic matter. Silurian exposures in the Podillya Region frequently include carbonate grainstones with bioherms containing corals, stromatoporoids and other fossils reflecting a shallow-water high-energy environment. These rocks alternate cyclically with dolomites of lagoonal origin and open-shelf argillaceous limestones (Łuczyński et al., 2016). K-bentonites occur mainly in the Malynivtsi and Rukshyn regional series that correlate with the Ludlow and Pridoli (Fig. 2). The thickness of these altered volcanic ash layers varies, commonly from a few millimetres to 20 cm, with a maximum of 50 cm. Correlation of the regional stratigraphy with global units has long been discussed. Carbon isotope studies by Kaljo et al. (2007, 2012) revealed

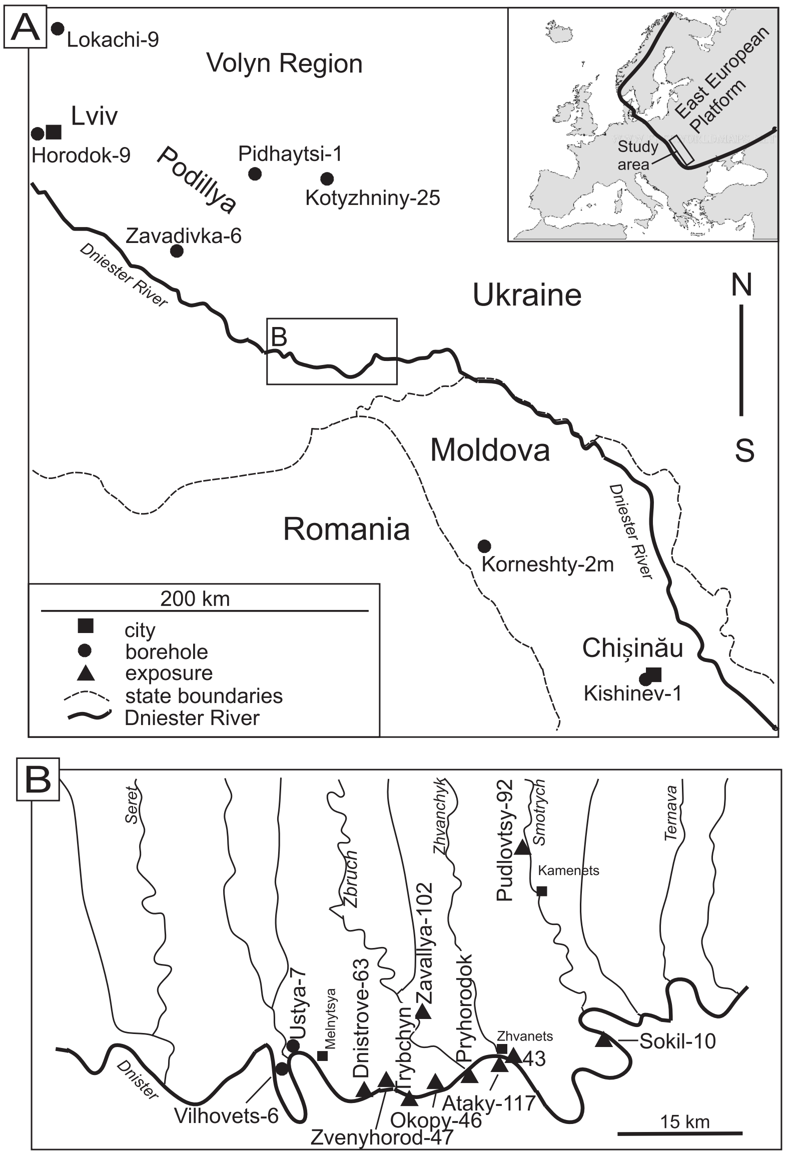

Fig. 1A – study area; B – exposure area of Silurian rocks along the Dniester River banks in Podillya

four positive excursions, previously known from other regions of the world, these giving significant confidence of correlation of the Ukrainian sections with global stratigraphy.

MATERIAL AND METHODS

K-bentonite samples collected by P.D. Tsegelnyuk in the 1970s and sent to E. Jürgenson (Estonia) for microscopic analysis were used in this study. Subsequently, these samples were stored in Estonian geological collections (http://geocollections.info), where sampling localities and stratigraphic information are available. Sixteen samples of this collection have been analysed using X-ray fluorescence (XRF) and X-ray diffractometry, the results being published in Kiipli et al. (2000b). In the present study the remaining 32 samples were analysed by standard XRF method for major and trace elements (Appendix*). For the calibration proficiency test, samples from the International Association of Geoanalysts and Estonian geochemical reference materials were used (Kiipli et al., 2000a). Accuracy of data is better than ±2% of concentration for major components and better than ±5% for immobile trace elements >20 ppm.

RESULTS

MAJOR COMPONENT GEOCHEMISTRY AND MINERALOGY OF THE K-BENTONITES

Volcanic ash consisting mostly of unstable glass rapidly changes in sedimentary environments, losing the primary igneous rock signatures (Huff et al., 1998; Kiipli et al., 2017). Data in the Appendix show low contents of SiO_2 compared with common acidic igneous rocks and high contents of Al_2O_3 and K_2O. Compositions of K-bentonites differ also from common sedimentary rocks. Plotting Ukrainian and Moldovian K-bentonites in a Al_2O_3-K_2O diagram, used in a study of Balto-Scandian K-bentonites (Kiipli et al., 2010), reveals similarly high Al_2O_3 and K_2O contents in both regions (Fig. 3) supporting a volcanic origin for the Ukrainian and Moldovian clay-rich interbeds. A volcanic origin was previously indicated by clay mineralogy (mixed layer illite-smectite) and the finding of volcanic phenocrysts (Huff et al., 2000). Grain fractions consist mostly of quartz and feldspar. Biotite and zircon phenocrysts dominate among heavy minerals, with rare apatite (Kiipli et al., 2000b).

GEOCHEMICAL CORRELATION

Due to the fundamental change in primary composition, only resistant phenocrysts like apatite (Batchelor and Evans, 2000) or immobile elements of bulk K-bentonite can be used in correlation. According to Kiipli et al. (2017) among the elements easily analysed by XRF in bulk bentonite, only Al_2O_3, TiO_2, Nb, Zr and Th have low enough mobility in sedimentary environments to be of use in correlation studies. Dai et al. (2017) mentioned that Ti shows mobility during alteration of volcanic ash in coal-bearing sequences. In the Baltic Basin our research team (Kiipli et al., 2014) noted also microscale mobility of Ti as authigenic anatase forming in K-bentonites with high TiO_2. Still we consider TiO_2 suitable for correlation studies if the thickness of layers exceeds some millimetres preventing significant escape of Ti. Correlation studies may be complicated by sporadic preservation of thin ash beds and by the similarity of

* Supplementary data associated with this article can be found, in the online version, at doi: 10.7306/gq.1580

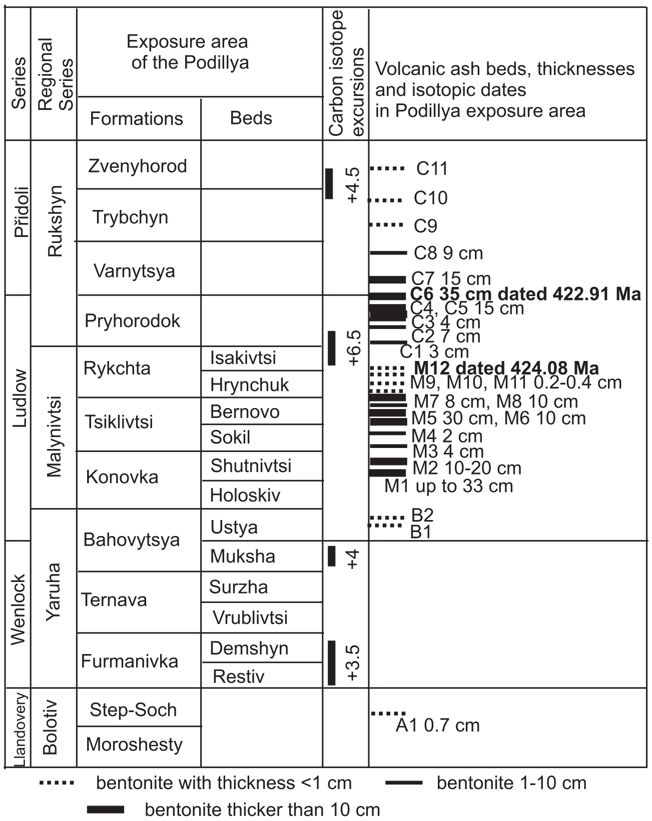

Fig. 2. Silurian stratigraphy in the exposure area in Podillya

Stratigraphic units, volcanic ash bed indices and thicknesses of K-bentonites are from Tsegelnyuk (1980a, b), Tsegelnyuk et al. (1983) and Kaljo et al. (2007). The stratigraphic position of carbon isotope excursions and correlation with global stratigraphy are given according to Kaljo et al. (2007, 2012). Isotopic dates are from Cramer et al. (2015)

trace element compositions in beds originating from different eruptions (Kiipli et al., 2010).

Correlation of the Malynivtsi Series (Ludlow) K-bentonites is shown in Figure 4. Field determinations of ash layer indices by P.D. Tsegelnyuk are marked within oval symbols and small bar charts visualise immobile element ratios. Element ratios were calculated following Kiipli et al. (2013): $TiO_2/Al_2O_3 \times 50$, $Zr[ppm]/Al_2O_3[\%] \times 0.1$, $Nb[ppm]/Al_2O_3[\%]$, $Th[ppm]/Al_2O_3[\%]$. To achieve comparable element ratios on the bar charts, coefficients were applied to some ratios. The perfect similarity of trace element spectra in different locations over a distance of 500 km for the M5 bentonite is remarkable, supporting previous correlation. Similar trace element spectra, that differ from those of other layers, occur also for the previously correlated M1, M2 and M9. Thus, the correlations in Figure 4 show that immobile trace element spectra can be used for seeking and demonstrating K-bentonite correlations in Ukrainian and Moldovian sections.

A more complicated situation is shown in Figure 5 where the Rukshyn Series (Upper Ludlow–Pridoli) ash beds occur. Using previous field determinations of bentonite correlations, marked by indices within oval symbols, we often discover clearly different trace element spectra at different localities. Considering the many volcanic eruptions and their sporadic preservation in sections it is obvious that some earlier preliminary correlations must be reassessed. Dotted lines in Figure 5 represent new correlations proposed on the basis of similarity of trace element spectra. For example C3 and C5 from the stratotype exposure area correlate most likely with volcanic ash beds previously assigned to higher stratigraphic levels in Moldova. This correlation

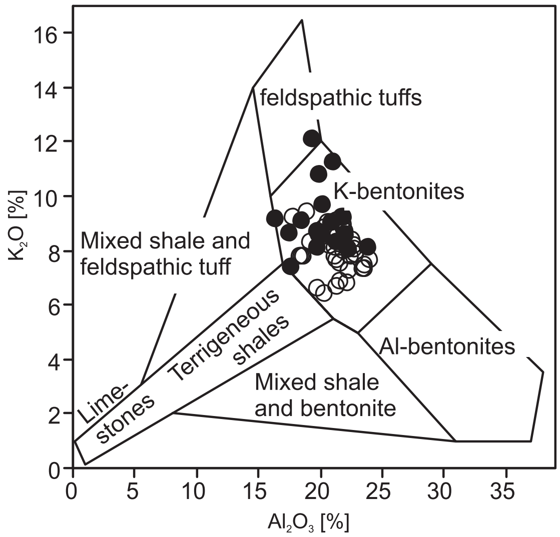

Fig. 3. Data from Silurian volcanic ash beds from the south-western part of the East European Platform on an Al_2O_3-K_2O chart, composed using data from the Baltic Basin

Black dots – M series K-bentonites,
circles – C series K-bentonites

remains provisional and needs further studies with geochemical data from more localities, both from exposures and from borehole cores, to achieve higher confidence.

INTERPRETATION OF SOURCE MAGMA

As with correlations, only immobile element ratios can be used for source magma interpretation, due to substantial diagenetic loss and gain of volcanic ash components. Using TiO_2/Al_2O_3 ratio as a fractionation index and Nb/Al_2O_3 ratio as an alkalinity index (Kiipli et al., 2020) the Silurian bentonites of Ukraine and Moldova clearly originated from rhyolitic source magmas (Fig. 6). This interpretation differs from a previous suggestion of trachyandesitic composition (Huff et al., 2000; Kiipli et al., 2000b) based on the Nb/Y-Zr/Ti diagram by Winchester and Floyd (1977). Rhyolitic source magma seems more probable, as studies have demonstrated mobility and loss of Y during the conversion of volcanic ash to bentonites (Christidis, 1998; Kiipli et al., 2017). Therefore use of the Nb/Y-Zr/Ti diagram frequently leads to the overestimation of the role of alkaline magmatism.

The temperature of granitic source magmas can be estimated using zircon saturation thermometry (Watson and Harrison, 1983). This is based on the solubility of zircon in felsic non-peralkaline melts being too low for complete dissolution of zircon during partial melting of most potential source rocks in the deep crust. Accordingly, zircon saturation is likely. In a zircon-saturated partial melt the concentration of zirconium strongly depends on the temperature and less so on the melt composition. In strongly altered volcanic rocks such as bentonites, possibilities for accurate calculation of source magma temperatures are limited. Kiipli et al. (2020) performed an approximate calibration of zircon saturation thermometry in the TiO_2/Al_2O_3-Zr/Al_2O_3 diagram. Although the method is not very precise, due to uncertainties rising from the possible presence of inherited zircons, and cases of unsaturated melts, it still enables provisional discrimination of low and high temperature

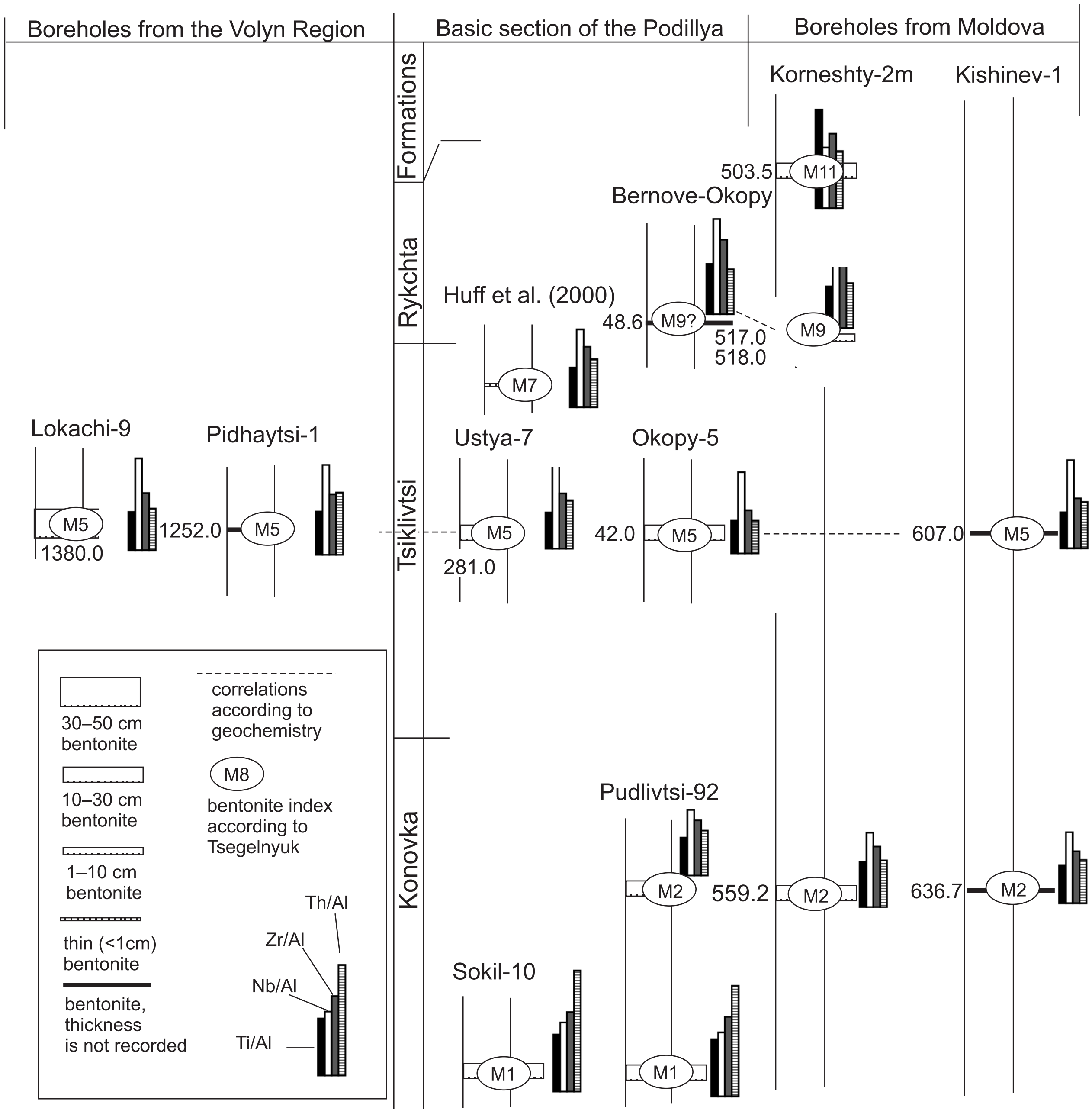

Fig. 4. Correlation of the Malynivtsi Series (Ludlow) K-bentonites

Previous correlations based on litho- and biostratigraphy (indeces inside ovals) are in a good correspondence with geochemical compositions (bar charts); for the details of bar chart calculation, see the text

non-peralkaline felsic source magmas. Plotting the Silurian bentonites of Ukraine and Moldova on this diagram reveals the low temperature nature of the magmatism (670–770°C, on average 720°C; Fig. 7). The temperature estimated from bulk rock composition refers to partial melting. Pre-eruption temperatures may have been somewhat lower. The abundance of biotite phenocrysts in the bentonites (Kiipli et al., 2000b) suggests a water-rich source magma. Low temperature and an abundance of water in the magmas indicate origin at a subduction zone, where hydrated oceanic crust carries water into the mantle causing a lowering of rock melting temperatures.

DISCUSSION ON VOLCANIC SOURCE AREAS AND RELATION TO PLATE MOVEMENTS

Silurian volcanism was common everywhere around the closing Paleozoic Iapetus Ocean (Huff et al., 2000). Towards the middle of the Ludlow Epoch, volcanic activity ended in most regions because of the final closure of the Iapetus Ocean and continental collision (Fig. 8). The southwestern margin of the Baltica Plate is exceptional in this respect – the volcanic record in strata starts from the end of the Wenlock, and Ludlow–Pridoli sections contain numerous interbeds of volcanic origin. It is rea-

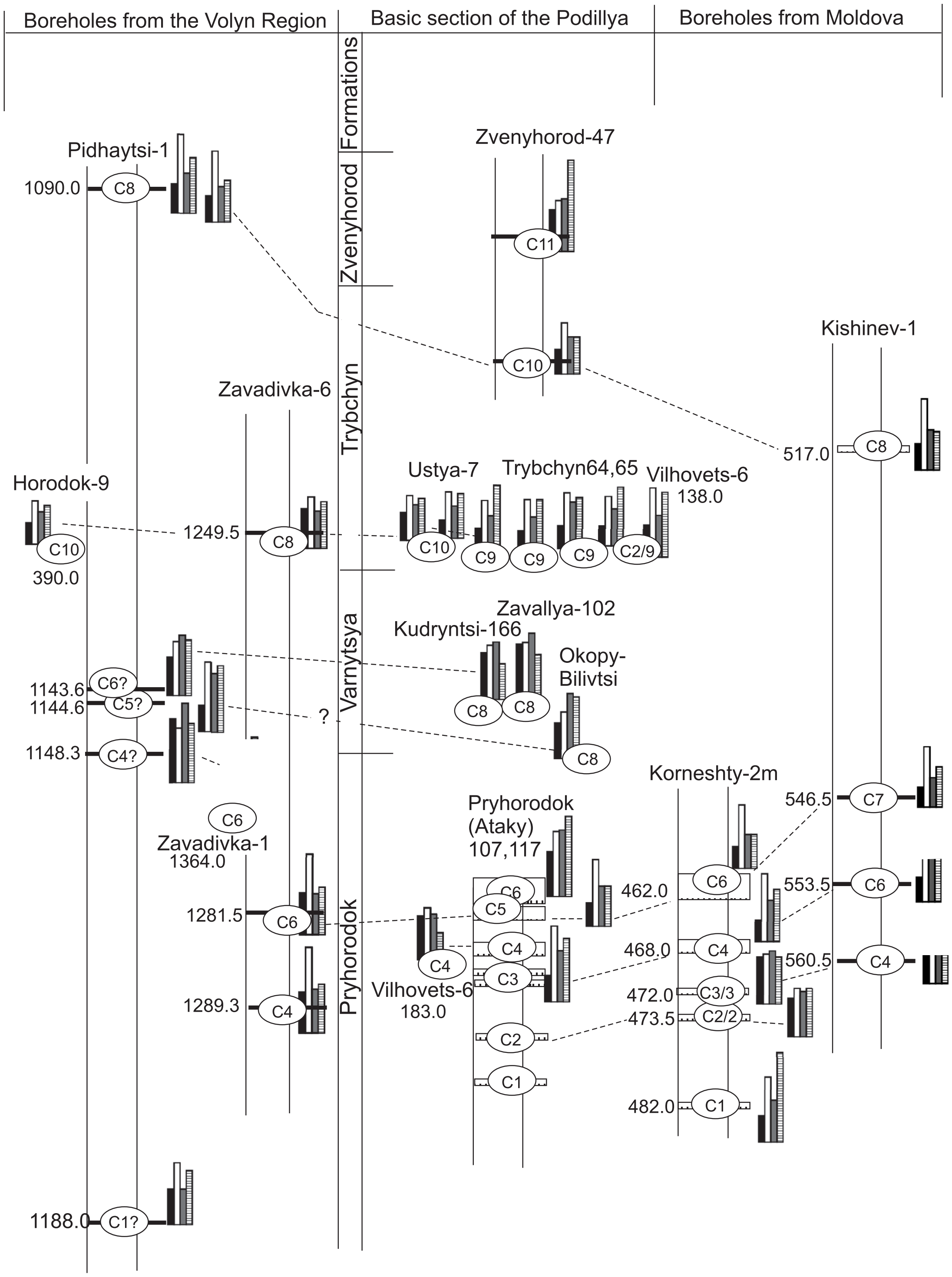

Fig. 5. Correlation of Rukshyn Series (Upper Ludlow–Pridoli) K-bentonites

For explanations see Figure 4; geochemistry suggest that the preliminary field determination of correlations (indices within ovals) needs correction

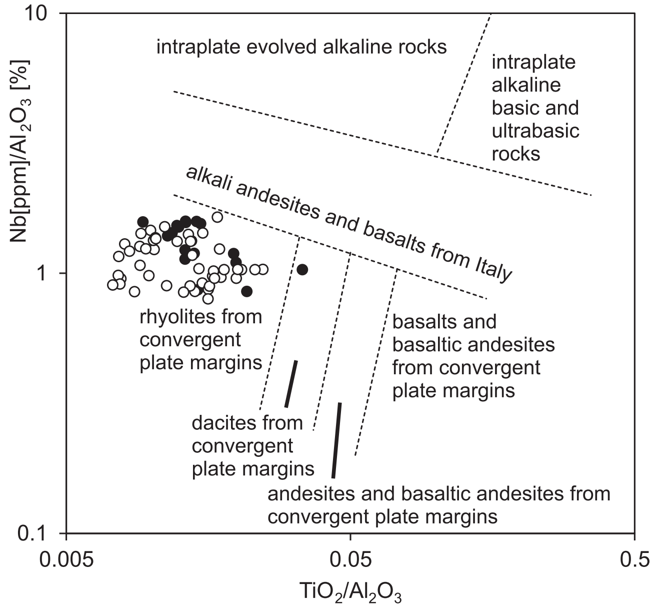

Fig. 6. Data from K-bentonites from the southwestern part of the East European Platform on a TiO_2/Al_2O_3-Nb[ppm]/Al_2O_3[%] chart (Kiipli et al., 2020)

Black dots – M series layers, circles – C series layers; immobile element ratios indicate rhyolitic source magmas

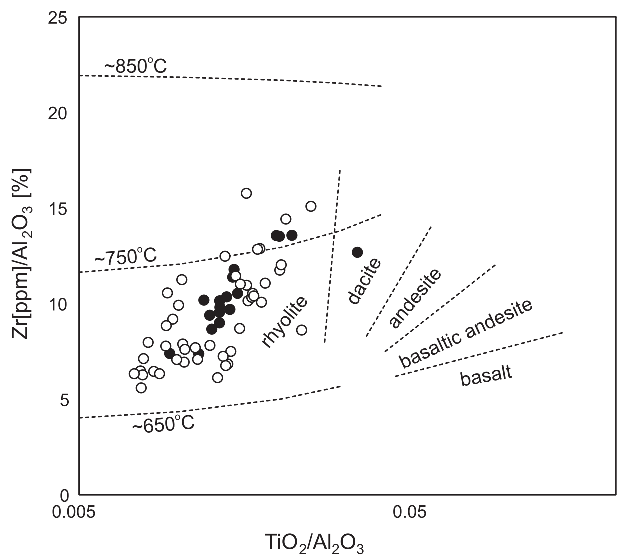

Fig. 7. Data from K-bentonites from the southwestern part of the East European Platform on a TiO_2/Al_2O_3-Zr[ppm]/Al_2O_3[%] chart (Kiipli et al., 2020)

For explanations see Figure 6

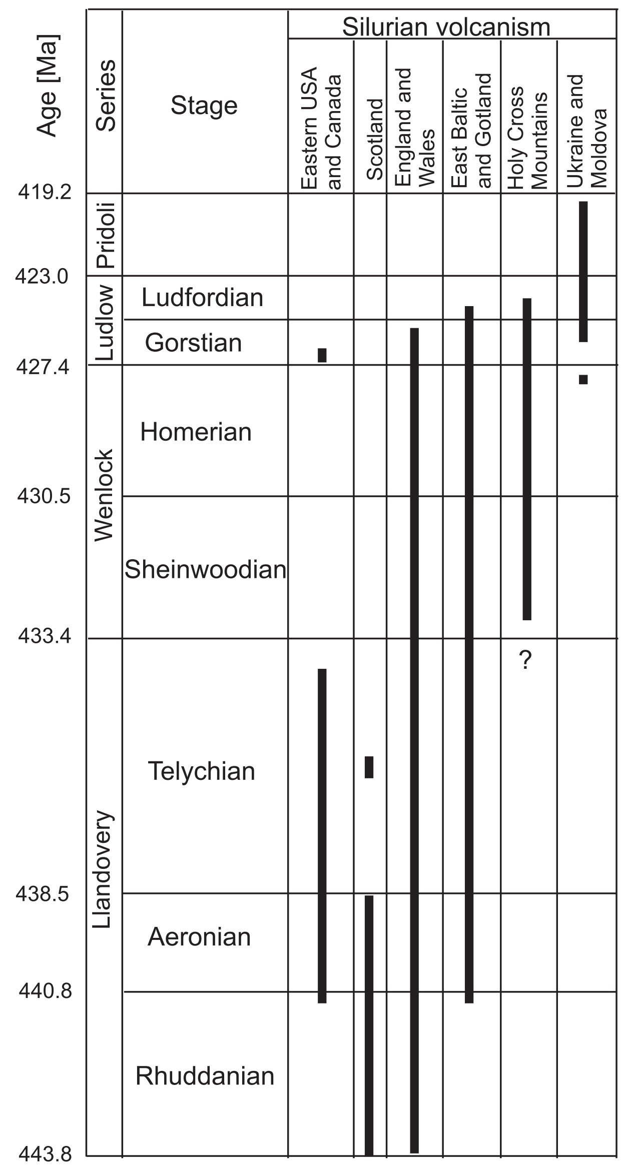

Fig. 8. Occurrence of volcanic ash beds in Silurian sections around the closing Iapetus Palaeoocean and at the southwestern margin of the Baltica palaeocontinent according to Huff et al. (2000) and Trela et al. (2018)

The volcanic record of the southwestern part of the East European Platform starts at the time when volcanism around the Iapetus Ocean ends

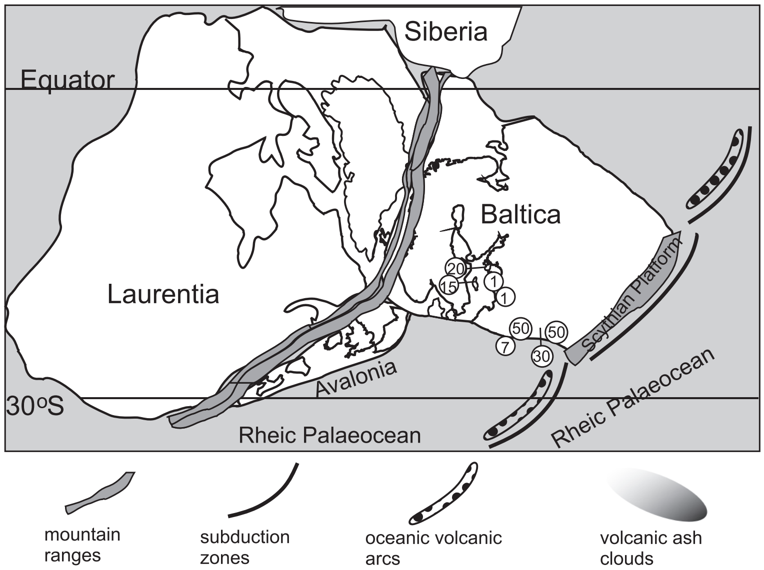

Fig. 9. Palaeogeography at the end of the Silurian Period

Baltica, Avalonia and Laurentia have collided and the Iapetus Palaeocean between them has closed (McKerrow et al., 1991; Golonka, 2002); continuation of extension in the southern Rheic Palaeocean forced the opening of a new subduction zone and triggered volcanism at the southeastern border of Baltica within the Scythian Platform that was being formed. Numbers inside white circles represent the maximum thickness [cm] of Ludlow-Pridoli K-bentonites in a particular region

sonable to suppose that extension in the Paleozoic Rheic Ocean, leading to the collision of Baltica and Avalonia with Laurentia, continued afterwards. Tectonic pressure caused the formation of a new subduction zone in the southeastern side of Baltica, supplying volcanic ash to nearby Late Silurian sedimentary environments (Fig. 9). The southeastern border of the East European Platform is adjoined by a narrow zone having mostly Paleozoic basement and termed the Scythian Platform (southern Ukraine and Russia), now deeply buried under younger deposits (Starostenko et al., 2015). The age of the metamorphosed basement in the Scythian Platform is not well-known. Golonka (2002) reported ages between 470–410 Ma, and Starostenko et al. (2015) suggested various ages from Ediacaran to Mesozoic, but mostly Variscan. The rhyolitic composition and the low temperature origin of the East Ukrainian K-bentonite source magmas indicate partial melting of continental crust. The volcanism most likely originated from subduction of Rheic oceanic crust under the forming Scythian Platform. Huff et al. (2000) also favoured a southern direction for the origin of volcanic ash and proposed the Mugodzhar arc in Turkey as a potential volcanic source.

Another potential source of volcanic material is the Central European Caledonides, albeit a less likely one as Ludlow age volcanic ash beds in the Holy Cross Mountains (directly to the west of Volyn) are relatively thin – mostly 2–5 cm, reaching 10 cm in one case (Trela et al., 2018). For comparison, the M-5 volcanic ash layer in the Lokachy-9 borehole core (north of Lviv city) is 50 cm thick (Tsegelnyuk, 1980a).

Silurian volcanic ashes in the Baltic Basin occur up to the Lower Ludlow (Kiipli et al., 2011). The thickness of the Lower Ludlow K-bentonites increases towards the north indicating a source from the Caledonides between Baltica and Laurentia. Pridoli age volcanic ashes have not been recorded within the Baltic Basin.

CONCLUSIONS

Geochemical correlation of K-bentonites of the Malynivtsi Series (Ludlow) is in good accordance with previous correlations basing on litho- and biostratigraphy. Geochemical data on K-bentonites of the Rukshyn Series (Ludlow–Pridoli) indicate that previous preliminary correlations need to be reassessed. The present study offers a new interpretation of tectono-magmatic processes at the margins of the Paleozoic Baltica plate using new analytical information. Source magmas of K-bentonites were low temperature (~720°C) rhyolites sourced from melting of continental crust. Volcanic sources were located probably within the developing Scythian Platform in a narrow zone at the south-eastern margin of the East European Platform.

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