Magnetic susceptibility variations in lower Paleozoic shales of the western Baltic Basin (northern Poland): A tool for regional stratigraphic correlations and the decoding of paleoenvironmental changes

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ABSTRACT

Magnetic susceptibility (MS) is a logging method commonly used for investigating lithostratigraphic features in marine sediments or petrophysical parameters. In this paper, an application of MS core logging as a tool identifying paleoenvironment and potential high organic matter content will be presented. The aim of the study was to define the relationship between magnetic methods, Rock-Eval pyrolysis data, and the results of natural gamma-ray wire-line logging. The MS logging was conducted on six drill cores from exploration boreholes in lower Paleozoic shales from the Baltic Basin, northern Poland. In each drill core, an interval of approximately 200 m was examined. The samples for laboratory measurements were taken from two drill cores more than 3500 m deep. The intervals of rock with variable amounts of organic matter were analyzed. The results indicate that MS variations in the analyzed rocks are strongly connected with the percent amount of chlorite and has a positive correlation with oxygen and bioturbation indices while having a negative correlation with total organic carbon. This relationship suggests that MS values were influenced by the redox conditions on the seabed in the early stages of diagenesis. Another important finding was that the MS value is associated with a ferroan chlorite amount. Therefore, it is critical to define the origin of chlorite.

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DATASHARE 131

Figures S1–S7 are available in an electronic version on the AAPG website (www.aapg.org/datashare) as Datashare 131.

When considering the thermal history of studied rocks (buried above 80°C), it is likely that chlorite was of a diagenetic origin. However, to confirm this assumption, Fe-rich clays that are precursors for diagenetic chlorite have to be defined.

INTRODUCTION

Low-field magnetic susceptibility (MS) measurements have become a common and widespread method in recognizing petrophysical properties of geological materials. This method has found an application in environmental and geological studies of sedimentary rocks as well as in paleoclimate reconstructions and thus allows researchers to better understand processes controlling the environment (e.g., Broding et al., 1952; Bloemendal et al., 1992; Stage, 2001; Potter, 2007; Da Silva et al., 2013).

Generally, the MS record reflects the total ferro-, para-, and diamagnetic compounds of the total rock volume. Further defining magnetic minerals characterized by different Fe phase (Fe^{2+}or Fe^{3+}) may help define redox conditions; for example, the occurrence of ferromagnetic hematite (characterized by Fe^{3+}) will suggest highly oxygenated conditions, whereas paramagnetic pyrite (with Fe^{2+}) will suggest the opposite. For proper interpretation of the MS signal from sedimentary rocks and magnetic composition, it is important to take into account that during cementation, diagenesis, and burial, there are many processes influencing the original composition: (1) sedimentary conditions like oxidation of bottom water, sedimentation rate, depth of the basin, and bioturbations; (2) early diagenetic processes like biogenic activity and organic matter (OM) decomposition; and (3) late changes in diagenesis including heating and chemical reactions like illitization or chloritization of smectite, fluid circulation, and maturation of OM. Previous investigations of organic-rich shales demonstrated that their MS is typically governed by phyllosilicates, which are the dominant components in these rocks (e.g., Chadima et al., 2004; Wenk et al., 2008; Heij et al., 2015; Niezabitowska et al., 2019b). However, the amount of paramagnetic minerals, such as pyrite or Fe-carbonate cement, may also be responsible for the MS variations (e.g., Schneider et al., 2004). Despite a large number of MS studies on organic-rich shales, the relationship between the amount of OM, processes controlling magnetic mineral composition, and MS still needs further investigation (e.g., Murdock et al., 2013; Kars et al., 2014; Manning and Elmore, 2015; Niezabitowska et al., 2019a).

Our previous studies provided detailed information about the magnetic mineral composition of the studied formations, which form a shale-gas exploration target discovered in central Europe (Niezabitowska et al., 2019a, b). The results showed the dominance of paramagnetic minerals, mostly phyllosilicates (mixed-layered illite-smectite and chlorite), with only small input of ferromagnetic phase, represented by low-titanium diagenetic magnetite and also detrital hematite present only in the beds with low content of OM (Niezabitowska et al., 2019a). In this paper, we examine Ordovician and Silurian rocks with variable amounts of OM from the western part of the Baltic Basin. The analyzed drill cores were sampled to recognize the potential of unconventional hydrocarbon sources in northern Poland (after Grotek, 1999; Poprawa, 2010; Tari et al., 2012; Karcz et al., 2013; Topór et al., 2017). The main goal of our study was to apply MS variations to determine lithological and sedimentological changes in lower Paleozoic shales and attempt to perform intercore stratigraphic correlations and relations between the MS results and various wireline logging and laboratory test results.

GEOLOGICAL FRAMEWORK

The studied area has experienced a multistage geotectonic evolution, represented by four structural stages separated by large hiatuses. The oldest part, the Proterozoic crystalline basement, which constitutes the East European craton, is overlain by the lower Paleozoic sedimentary cover (Ediacaran to Silurian), Permian–Mesozoic cover, and Cenozoic cover in the upper part (e.g., McCann, 2008). Each sedimentary cover differs from others by geotectonic regimes and paleogeography that occurred during deposition. Generally, all formations from Ediacaran to Cenozoic are not tectonically folded and have horizontal bedding. The studied rocks were deposited in the Baltic Basin, which is interpreted as an elongated sedimentary basin located along the present southwestern margin of Baltica (e.g., Geyer et al., 2008). The analyzed samples were collected in the Peribaltic syneclise from different facies starting from Upper Ordovician to Wenlock (Silurian) (Figure 1). Peribaltic syneclise is interpreted as an epicontinental depression developed during the Wenlock (Silurian) to the late Caledonian stage (e.g., Suwejzdis, 1968). It is filled by Ediacaran to Silurian deposits (e.g., Geyer et al., 2008).

During the Middle to Upper Ordovician and the Silurian, the Baltica continent was situated between 10°S and 45°S (e.g., Scotese, 2001; Verniers et al., 2008; Torsvik et al., 2017). At this time, the Avalonia microcontinent docked progressively to the southern margin of Baltica, which led to the development of the Caledonian orogenic wedge and the associated foredeep basin (e.g., Verniers et al., 2008). This changed the character of subsidence in the Baltic Basin from passive margin regime to flexural bending of the present southwestern part of Baltica that increased the subsidence rate (Poprawa et al., 1999; Poprawa, 2010). The formation of the Baltic Basin, as a pericratonic sedimentary basin, was controlled by the approaching front of the Caledonian orogeny through the Middle–Late Ordovician and Silurian (Jaworowski, 2002; Modliński and Podhalańska, 2010, and references therein). The Baltic Basin sediments exhibit induced distinct zonation of lithofacies (e.g., Modliński, 1976; Modliński and Podhalańska, 2010). Therefore, the major source of detrital material deposited in the basin was the Caledonian deformation front and related accretionary prism, which dominated the sedimentation in the westward part of the basin. However, small impact of carbonate inputs eastward were observed in the Prabuty and Pelplin Formations (e.g., Modliński et al., 2006). In the eastern part, the siliciclastic deposition was replaced by carbonate input (e.g., Lazauskiene et al., 2003; Calner, 2005). The examined rocks were deposited in the present western part of the Baltic Basin, in the siliciclastic zone with episodic carbonate input, and they constitute continuous lithofacies profile of several formations: Kopalino Formation (upper Arenig to the upper Llanvirn, Ordovician), Sasino Formation (the lowermost Llanvirn to uppermost Caradoc, Ordovician), Prabuty Formation (upper Ashgill, Ordivician), Jantar Formation (Llandovery, Silurian), Pasłęk Formation (Wenlock, Silurian), and Pelplin Formation (Wenlock, Silurian) (after Modliński et al., 2006).

The rocks in the Polish part of the Baltic Basin from a depth interval of 2400–4300 m show vitrinite reflectance values of maximum 1.42% (Karcz et al., 2013) corresponding to the maximum temperature of 150°C. According to Mastalerz et al. (2013), these temperatures show that the rocks were buried up to the wet gas diagenetic or catagenetic stage, which occurred before the end of the Devonian (Grotek, 1999; Środoń and Clauer, 2001). The burial history has a significant impact on the mineralogical composition of analyzed shales, in which processes like illitization of smectite were identified (e.g., Środoń and Clauer, 2001).

Burial history of the present western part of the Baltic Basin remains the subject of extensive debate

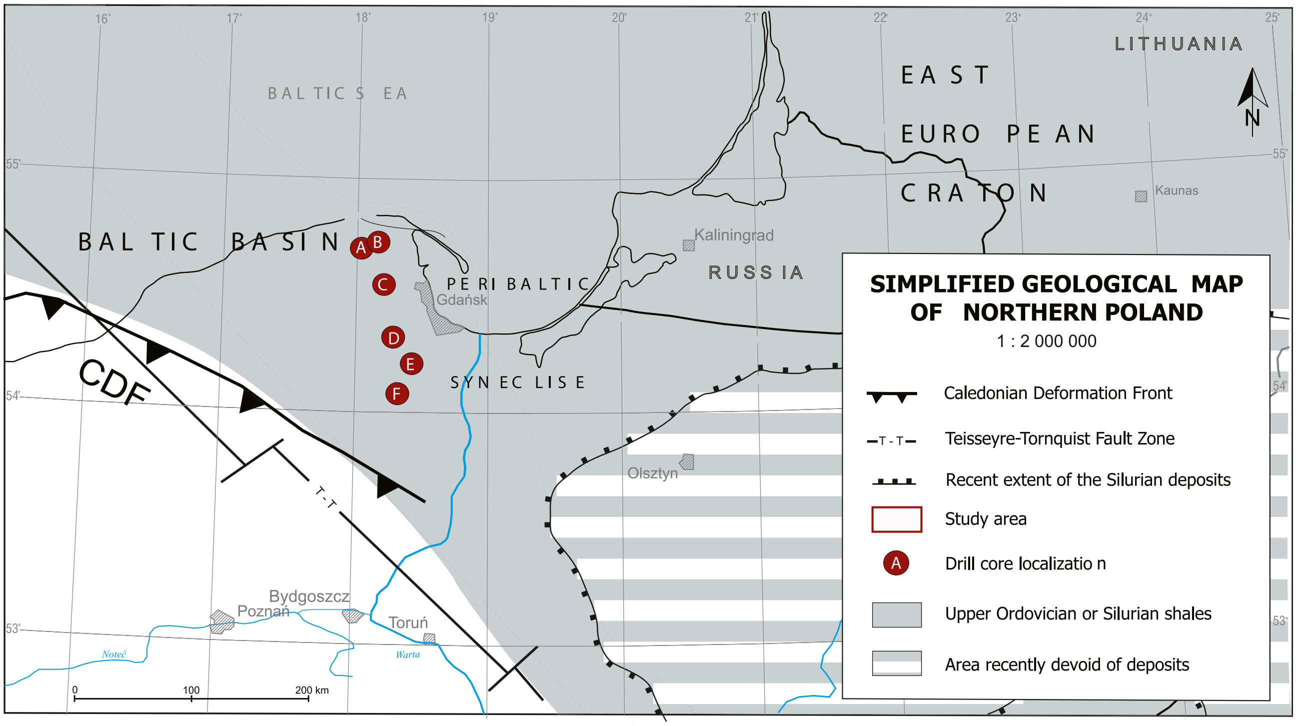

Figure 1. Simplified tectonic map of northeastern Poland (modified after Modliński and Podhalańska, 2010) with the locations of the analyzed drill cores. CDF = Caledonian deformation front (after Grad et al., 2002).

(e.g., Karnkowski, 2003; Poprawa et al., 2005, 2010; Wróbel and Kosakowski, 2010). It is assumed that the major thermal event resulted from the Variscian collision, which has led to the generation of hydrocarbons upon the maximum paleotemperatures (e.g., Wróbel and Kosakowski, 2010). However, it is likely that during the late Mesozoic the geothermal gradient increased, contributing to further generation of oil and gas (e.g., Poprawa et al., 2005). The actual timing and origin of maximum paleotemperatures remain unclear, and there is no consensus on whether it was a result of simple burial or burial combined with hot fluids circulation (Witkowski, 1993; Karnkowski, 2003; Poprawa et al., 2005; Somelar et al., 2010).

The lithostratigraphic units for the Ordovician–Silurian section of the Baltic Basin (Figure 2) have been extensively described by Bednarczyk (1996), Modliński and Szymański (1997), Lazauskiene et al. (2003), Modliński et al. (2006), Modliński and Podhalańska (2010), and Porębski and Podhalańska (2019) and earlier by Modliński (1982) and Tomczyk (1989). These divisions are well known, and they are easily recognizable in the profiles across the basin; therefore, we decided to use the division, presented in Figure 2, in our study.

MATERIALS AND METHODS

MS Variations through Drill Cores

The MS logging was conducted on six drill cores from exploration wells, labeled as A, B, C, D, E, and F (Figure 1), located approximately 20 km apart from each other. In all drill cores, the measurements were performed within the interval from Upper Ordovician (Katian, Hirnantian) formations to lower Silurian (Llandovery, Wenlock) formations. The MS measurements were performed with an MS meter SM30 (ZH Instruments, Czech Republic), with a sensitivity of 1×10^{-7} International System Units (SI) and operating frequency of 8 kHz. In each drill core, an interval from approximately tens to 200 m was examined, depending on the length of the Ordovician–Silurian cored intervals, core recovery, and quality. Each of the measured parts of the drill core was taken out of the box and measured in a metals-free environment to avoid interferences. The resolution

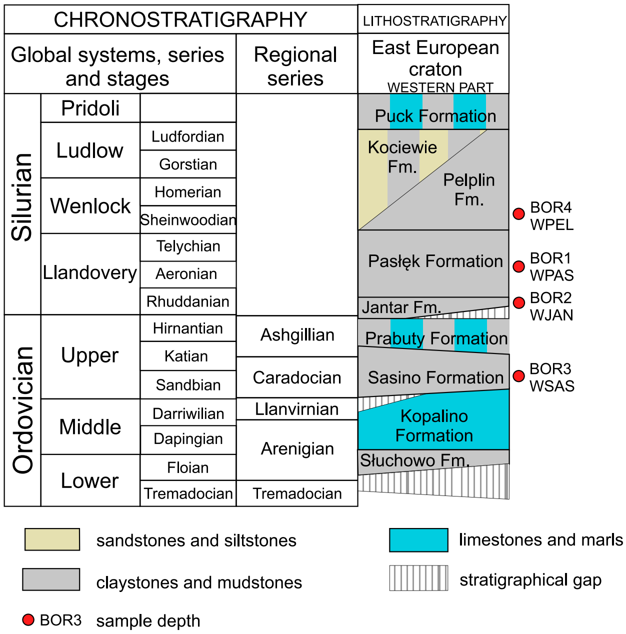

Figure 2. The stratigraphic divisions of the lower Paleozoic in the Polish part of the Baltic Basin; modified after Modliński and Podhalańska (2010). BOR = drill core D; Fm. = Formation; WJAN = Jantar Formation, drill core F; WPAS = Pasłęk Formation, F drill core; WPEL = Pelplin Formation, F drill core; WSAS = Sasino Formation, F drill core.

of the measurements was approximately 3 to 4 measurements per 1 m of drill core. Each MS measurement was repeated at least twice for each measurement point, to monitor measurement precision. To verify the correctness of MS results performed with the SM30 meter, the measurements of one selected profile were repeated with the MS3 meter (Bartington, United Kingdom), with a sensitivity of 2×10^{-6} SI.

Rock Magnetic Measurements

To identify magnetic compounds (ferro- and paramagnetic minerals) present in the facies Sasino, Prabuty, and Pasłęk, rock magnetic measurements such as (1) acquisition of isothermal remnant magnetization (IRM) experiments (defining coercivity), (2) hysteresis analyzes providing information about coercivity and remanence, and (3) temperature variation of MS (distinguishing ferro- and paramagnetic content) were initiated. These experiments were carried out on 134 specimens of different types (cylindrical, chips, and powder) collected from two drill cores, D and F. The samples were prepared from 6-cm-long intervals of the Pasłęk, Sasino, Pelplin, and Jantar Formations obtained from Polskie Górnictwo Naftowe i Gazownictwo SA (PGNiG). All magnetic experiments were investigated in the paleomagnetic laboratory of the Institute of Geophysics, Polish Academy of Sciences, Warsaw, Poland.

For the IRM and MS purposes, 50 standard volume-normalized cylinder specimens of 26×22 mm in size (diameter × height) were prepared. The specimens were collected from all available intervals. The IRM experiments were performed on 18 specimens over 8 steps up to 3 T. The samples were magnetized using an MMPM1 pulse magnetizer by Magnetic Measurements (United Kingdom) and measured in a 2G SQUID cryogenic magnetometer (noise level: $\sim 10^{-10}$ Am^2). To compare the values of MS obtained from the MS profiling through the drill cores, low-field MS measurements were performed in the laboratory on 50 cylindrical volume-normalized specimens collected from 4 analyzed facies. The experiments were carried out with an MFK1-FA (sensitivity 2×10^{-8} SI) by Agico Instruments (Jelínek and Pokorný, 1997). The MS was measured in a 200 A/m field at room temperature.

The hysteresis studies were conducted using a vibration magnetometer MicroMag AGM (noise level: $\sim 10^{-7}$ Am^2). Measured 32 mass-normalized specimens were chips of rock weighing ~20 mg. The slope correction for the paramagnetic phase was applied according to the standard MicroMag AGFM correction setting (at 70% of the highest field).

Additionally, the temperature variation of MS using the Kappabridge KLY-3S of instruments (sensitivity: $\sim 2 \times 10^{-8}$ SI, accuracy: 0.3%) combined with the CS-2/CS-L furnace apparatus of Agico was observed on 22 powder specimens in air atmosphere. The raw data were corrected for the empty furnace background measurements. To assess the percentage contributions of ferromagnetic minerals to the composition of the samples, we applied the method of Hrouda (1994) and Hrouda et al. (1997) through fitting a hyperbola to the initial part of a thermomagnetic curve (50°C–250°C temperature range) using the least-squares method. The calculations were conducted in the instruments Cureval8 software.

Lithosedimentological and Mineralogical Analyses

Macroscopic observations on drill cores were focused on establishing typical sedimentary features, for example, types of lamination, types of bioturbation and their index (after Reineck, 1967; Taylor and Goldring, 1993), carbonate concretions, the presence of pyroclastic layers, and the occurrence of pyrite, as well as fossils abundance.

The mineralogical data provided from industry were used in correlations and interpretations. Thanks to collaboration with PGNiG, the following data were obtained. (1) Wire-log data corresponding to clay contribution: gamma-ray logging using gamma-ray for potassium and thorium and gamma-ray total. (2) Results on core samples, such as mineral composition analyzed with x-ray diffraction (XRD), providing quartz, clay minerals, dolomite, and calcite or accessory minerals like pyrite, halite, or anhydrite contents. Detailed quantitative mineral compositions were determined for 120 samples from drill core B. (3) Rock-Eval pyrolysis on core samples, providing useful parameters: total organic carbon (*TOC*) and oxygen index (*OI*) corresponding to oxygen content in OM, thus a potential proxy for oxidizing conditions (e.g., Anderson et al., 1981; Słowakiewicz et al., 2015).

Parameters Relationship Analyses

Variation of MS along the sedimentary profile was compared with variation of *TOC* and *OI* in several data sets measured continuously on a core (MS variation) or selected samples. These data sets come from the Rock-Eval pyrolysis, which is an analytical technique that allows tracking changes in OM's provenance, maturation and degradation, XRD analysis (mineral phase contents; see Topór et al., 2017), and bulk rock chemical composition data (coming from reported mineral proportions and electron microprobe analyses). Note that these data are point based and were received from small core samples; therefore, their resolution is lower than MS measurements. Additionally, MS results were compared with the natural gamma-ray wire-line logging profile after data juxtaposition based on coring and logging depths. For one core, the variation of bioturbation index (BI), observed during sedimentological profiling, was also compared with MS data. The BI directly reflects trace fossil density and the amount of trace fossil overlap (Reineck, 1963). All analyzed and compared data were not collected from exactly the same points; however, to statistically evaluate their relationships, common statistical tools like cross-correlation plots were performed. All presented curves are based on drill depths. The Rock-Eval, gamma-ray logging, as well as XRD data and chemical analyses were provided by the Polish Geological Institute–National Research Institute (NRI) and the Oil and Gas Institute–NRI within the ShaleMech project.

RESULTS

Samples Measurements of MS

When comparing MS values from two intervals of the same facies, the Pelplin Formation, both already published (Niezabitowska et al., 2019b) and new data, we observe similar values. The values for mudstones collected from the middle part of the Pelplin Formation (Figure S1, supplementary material available as AAPG Datashare 131 at www.aapg.org/datashare) range from 200–280 × 10^{-6} SI (Niezabitowska et al., 2019b), whereas in deeper intervals of the same facies, the values are slightly smaller, staying within the 180–216 × 10^{-6} SI range (this study). Visible abrupt reduction of MS in profile (in the Pelplin Formation) corresponds to carbonate concretions, whose MS is within the 110–150 × 10^{-6} SI range (Figure S1). The highest values of MS were observed in the samples collected at 5-cm intervals from the Pasłęk Formation (Figure S1), as they reached 336 × 10^{-6} SI in both drill cores. In turn, in the deeper Jantar Formation and the Sasino Formation, MS strongly decreased, especially in drill core F, where MS stayed in the 70–100 × 10^{-6} SI range. However, in drill core D, these corresponding values are slightly higher (136–175 × 10^{-6}).

In general, these results correspond closely to MS data measured along the analyzed drill cores in the field (Figure S1, supplementary material available as AAPG Datashare 131 at www.aapg.org/datashare). However, because of the curvature of the cylindrical drill core, which implied measurements of a nonflat plane, all MS values from the field have to be corrected with a factor of approximately 1.8 to be compared to the results from the laboratory. However, as the present study focused mostly on MS variations determined by changing of environment, we did not apply the correction on MS profile values.

Rock Magnetic Measurements

IRM Acquisition Curves and Hysteresis Loops

In all types of rocks, the results of IRM show a strong increase of magnetization below 0.5 T, which documents the clear dominance of low-coercivity minerals. In higher values of the applied field (0.5–1 T), an increase of IRM curves becomes less rapid, indicating the occurrence of small amounts of medium-coercivity minerals. In general, complete flattening of all IRM curves documents the absence of high-coercivity minerals, such as goethite or hematite. Exceptions are the samples from the Pasłęk Formation (orange) and the Pelplin Formation (yellow), where the IRM curves are not saturated at 3 T (Figure S2, supplementary material available as AAPG Datashare 131 at www.aapg.org/datashare). Interestingly, in these two formations, the magnetization reached higher values than in the Sasino Formation (blue) or in the Jantar Formation (green), suggesting larger amounts of a low-coercivity component (Figure S2).

The shape of the hysteresis loops for all samples indicates dominance of paramagnetic minerals, with a small contribution of ferromagnetics, which is clearly visible after correction for a paramagnetic phase. Fast saturation of corrected loops, indicating the presence of low-coercivity minerals, is in line with coercivity values generally not exceeding 10 mT (Table 1). The values of saturation magnetization after correction for paramagnetic minerals (M_s) range from 340 to 2400 $\mu Am^2/kg$ for each sample; however, in each formation these values are quite homogenous (Table 1). Magnetic remanence (M_r) is similar for most of the formations and is equal to approximately 40 $\mu Am^2/kg$. An interesting exception is in the Sasino Formation from drill core D, with a single value of 379.9 $\mu Am^2/kg$, characterized by high (31%) ferromagnetic content associated with pyrite concretion. Excluding this kind of anomaly, the ferromagnetic contribution in each formation does not exceed 15% of the total MS (Table 1). Considering the hysteresis parameters of the analyzed formations, the differences are visible in M_s and M_r parameters, and the ferromagnetic to paramagnetic proportion, that are generally higher in the Sasino and Pasłęk Formations.

Temperature Variations of MS

The results of thermal variation of MS are in line with the outcome from hysteresis analysis. We obtained similar results for all the analyzed formations. The initial part of the curve has mostly a hyperbolic to flat shape, which can indicate the dominance of paramagnetic minerals with ferromagnetic input (Figure S3, supplementary material available as AAPG Datashare 131 at www.aapg.org/datashare). In all the examined samples at temperatures greater than 400°C, thermochemical reactions corresponding with the formation of new magnetite were observed. We applied the separation method of Hrouda (1994) and Hrouda et al. (1997), which allowed us to constrain the proportion between ferromagnets and paramagnets. The analyses show that MS of the studied rocks (in all formations) is controlled by paramagnetic minerals with a small input of ferromagnetic minerals, not exceeding 15%.

MS Logs

Despite some negligible differences in values of MS, the variation of curves obtained from two independent experiments (using SM30 or MS3 sensor) correlate well (Figure S4, supplementary material available as AAPG Datashare 131 at www.aapg.org/datashare). Statistical analysis for more than 150 measurement points (exactly the same depths for both methods) shows R^2 determination coefficient (DC) equals 0.83 for linear fit. The number of analyses of MS variations is significant and reliable; thus, we based our interpretations on them. The results of MS are presented in 10^{-6} SI (see Figure 3); however, these values should be treated as relative values because they do not reflect the actual values of MS in the analyzed rock (factor 1.8 corrects the exact values of MS, as described earlier in the Results section).

At first, the MS curves from all analyzed drill cores were compared in between separated lithostratigraphic units (Figure 3). The boundary between the top of the marl and claystone in the Prabuty Formation and the base of the claystone Jantar Formation was adopted as the main reference line because it is isochronous in the basin. This boundary line also corresponds with the chronostratigraphic Ordovician–Silurian boundary (Modliński and Podhalańska, 2010). In each MS log, we observed the repeatability of general trends, which can be assigned to specific lithostratigraphic units. An example is the pronounced zone of decline in susceptibility corresponding with bitumen claystone in the Jantar Formation (Figure 3, green area). Moreover, we can distinguish intervals with the same behavior of MS curve in each drill core, for instance, increasing of MS in the base of Pasłęk Formation, further decreasing, once again increasing, and then a decreasing trend close to the boundary with Pelplin Formation (Figure 3, purple and yellow parts).

MS Log versus Lithosedimentological Changes in the Analyzed Formations

As initially observed, the analyzed rocks are generally homogenous throughout the formations; however, detailed analysis shows subtle changes in lithology, such as tuff intercalations, concretions abundance, as well as variations of carbonate (even in centimeter or millimeter scale) that allowed understanding of the

Table 1. The Hysteresis Parameters for 6-cm Intervals for all the Analyzed Facies from Two Drill Cores, D and F

				Values			
Drill Core	Formation	Depth, m	Sample	M_s, μAm²/kg	M_r, μAm²/kg	B_c, mT	FC, %
Drill core D	Pelplin	3623.84–3623.90	BOR41	341.2	31	7.8	6.2
			BOR42	675.2	52.2	6.4	6.8
			BOR43	630.1	33.7	6.6	6
			BOR44	782.4	64.5	7.9	7.5
	Pasłęk	3639.69–3639.75	BOR11	722.9	12	11.9	7.6
			BOR12	1203	54.3	4.7	5.7
			BOR13	987.4	47.7	5.2	5.7
			BOR14	1516	48.8	4.1	21.3
	Jantar	3683.25–3683.31	BOR21	670.5	36	7.4	7.2
			BOR22	635.5	40.6	7.3	7.3
			BOR23	530.4	38.3	8.1	6.6
			BOR24	554.3	35.4	8	7.3
	Sasino	3702.51–3702.60	BOR31	1640	45.1	4	17.2
			BOR32	2399	379.9	4.9	30.5
			BOR33	749.7	38.4	4.1	4.4
			BOR34	535.1	36.9	6.2	6.5
Drill core F	Pelplin	3897.85–3897.91	WPELP1	579.5	30.5	5.6	6.5
			WPELP2	607.6	42.1	7.2	7.2
			WPELP3	582.1	31.1	4.2	6.5
			WPELP4	489.4	21.8	5.2	6.2
	Pasłęk	3918.00–3918.06	WPAS1	1230	57.6	5.8	7.1
			WPAS2	692.4	28.4	5.6	4.1
			WPAS3	974.8	46.3	8.5	5.2
			WPAS4	521.9	37.8	7.8	9
	Jantar	3944.52–3944.57	WJAN1	435.6	37.6	8.1	16.4
			WJAN2	476.4	35.9	8.4	10.9
			WJAN3	663.5	56.1	6.3	14.6
			WJAN4	503.5	46.1	8.1	12.1
	Sasino	3960.00–3960.06	WSAS1	554.6	39.6	7.8	11.2
			WSAS2	494.6	34.9	6.3	11.4
			WSAS3	435.5	26.3	6.9	9.6
			WSAS4	697.8	62.6	10	15.2

Ferromagnetic contribution (FC) is calculated from the initial slope after (ferromagnetic susceptibility) and before correction for paramagnetic minerals (total susceptibility).
Abbreviations: B_c = coercivity; BOR = drill core D; M_r = magnetic remanence; M_s = saturation magnetization after correction for paramagnetic minerals; WJAN = Jantar Formation, WPAS = Pasłęk Formation, WPEL = Pelplin Formation, WSAS= Sasino Formation.

variability of the MS curve and how it is linked to the general trend, determined by lithology, or related to local "sedimentary events" like tuff layers, fossils, or concretions (see Figure 4).

The detailed comparison between sedimentological characteristics of the formations and the MS curve shape started from the Ordovician Sasino Formation (shales), which stratigraphically belongs to the Sandbian to Katian (see Figure 2). Lithological and sedimentological observations show that the whole formation in all the analyzed drill cores can be subdivided into three parts, which are also visible on the MS curve (Figures 4E, 5A, 6A). The bottom of the formation is erosive, covered by a few meters of laminated or massive argillaceous mudstones, dispersed fine-grained pyrite concretions, and large fauna abundance (mostly graptolites). The OM content is high in this formation; however, there are significant intercalations (several centimeters to decimeters) of mudstones with characteristic dark bioturbations in which *T*OC decreases dramatically (Figures 5, 6; Figures S5, S6, supplementary material available as AAPG Datashare 131 at www.aapg.org/datashare). The MS value in those dark bioturbated mudstones is relatively high and decreases in the laminations enriched in OM and fine-grained pyrite. In the middle part of the Sasino Formation, there are thick layers of tuff. Here the MS curve has lower values comparing to the adjacent intervals. In the upper part of the formation, bituminous argillaceous mudstones with parallel lamination occur. They are characterized by an abundance of fine pyrite concretions, with graptolite faunas that appear once again. This part shows the highest OM content from the whole formation (Figures 5, 6; Figures S5, S6, supplementary material available as AAPG Datashare 131 at www.aapg.org/datashare) and low MS values.

The Prabuty Formation (marls and shales) is the last Ordovician lithostratigraphic unit and includes mudstones, marls, and limestones. In all the investigated profiles, the formation can be divided in two parts: (1) the lower part contains mostly carbonate mudstones and marls and (2) the upper part contains pelitic limestones and detritic and organodetritic limestones. The complicated shape of the MS curve corresponds to the rapid lithological changes in the profile (Figure 4C). The Prabuty Formation is characterized by the highest value of MS that appears within the massive grayish mudstone with no visible structures to the naked eye. The lower part of the MS curve with higher values corresponds to the massive mudstones and marls. Rapid decreases of the MS curve appear in more calcareous carbonates, including pelitic limestones or detritic limestones, which are clearly visible in the upper part of the Prabuty Formation.

The upper boundary is erosive, and the Prabuty Formation is covered by the transgressive Jantar Formation (bituminous black claystone), which is the first Silurian unit. The Jantar Formation contains bituminous black argillaceous mudstones. The monotonous black to brownish-black, noncalcareous mudstones are massive or thin laminated with almost no bioturbation. They contain a large abundance of fine pyrite dispersed in the matrix or arranged along lamination. The whole rock is full of graptolitic fauna and enriched in OM (Figure 4D). The MS values in this part of the profile are low, and the shape of the MS curve is stable. From the bottom of the formation to the middle part, there is a visible decrease of MS. Only one spectacular peak is observed within a layer characterized by an enrichment of very small dispersed pyrites.

The Jantar Formation passes into the Pasłęk Formation (shales) of Llandovery age. The formation contains alternate thin, layered, grayish-black mudstones and greenish massive mudstones, sometimes cemented by dolomite. Fine-grained postdiagenetic pyrite concretions arranged along lamination can be easily observed. The lowest part of the formation is enriched in OM.

The MS curve in the Pasłęk Formation is strongly diversified. The bottom part is characterized by a gradual increase with two characteristic high positive peaks (Figures 3, 4E, 5, 6). Comparing to the lithology and sedimentary structures within, the first peak corresponds to a carbonate layer, but the second one occurs in the laminated mudstones and remains enigmatic. The middle part of the Pasłęk Formation is characterized by various but high MS values. When the regular changes in lithology from dark (grayish-black) argillaceous laminated mudstones to greenish, massive bioturbated mudstones occur, the MS curve increases with no diagnostic peaks. The highest peaks are in the homogenous, massive gray mudstones with no visible structures save for phosphate concretions (1–3 cm in diameter). In the upper part of the Pasłęk Formation, the MS curve decreases gradually within the alternating dark-gray to green layers of mudstones. In this part of the profile, the dark laminated mudstones, with characteristic lenticular textures within,

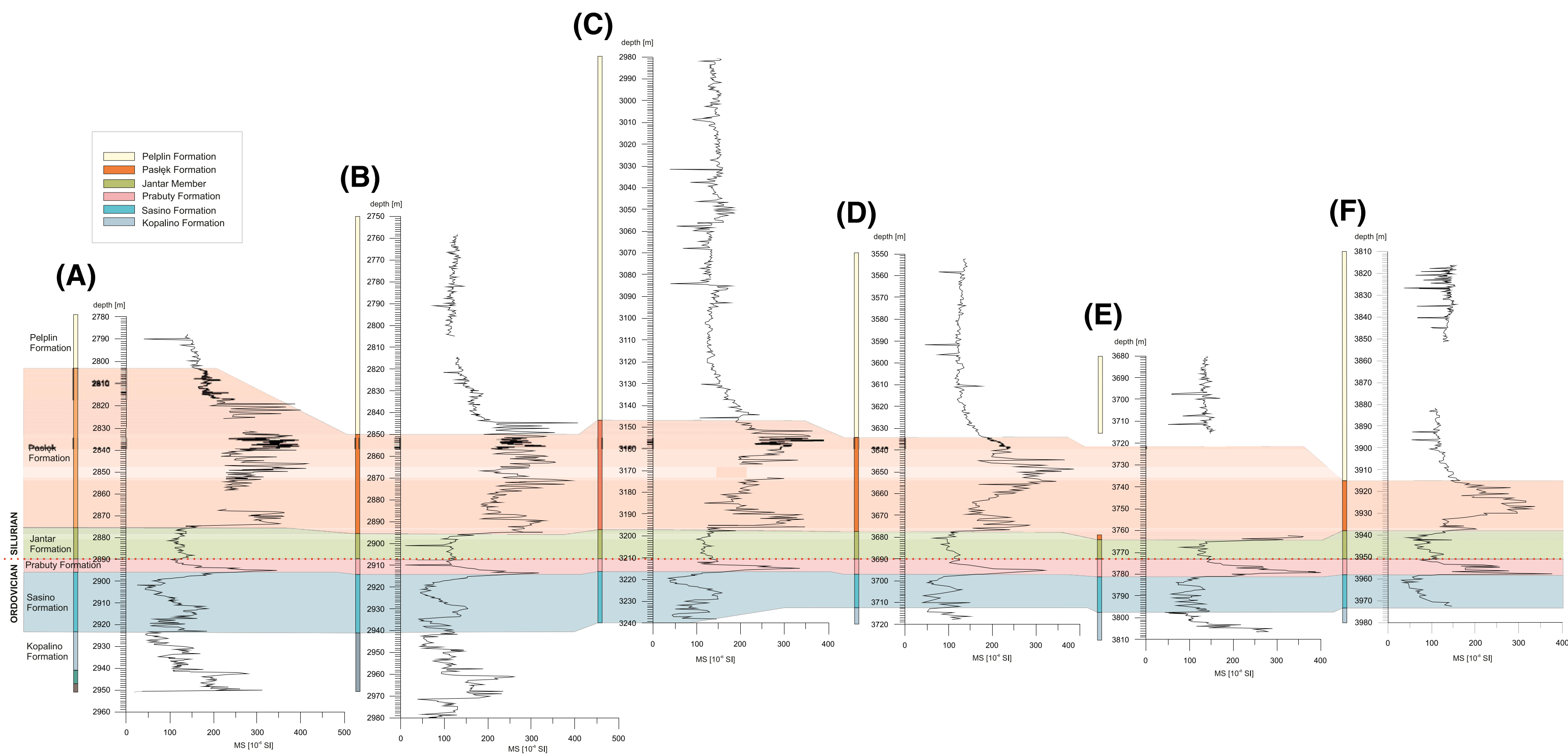

Figure 3. Magnetic susceptibility (MS) logs compared with the litho-sedimentological profile of all the analyzed drill cores: (A) drill core A, (B) drill core B, (C) drill core C, (D) drill core D, (E) drill core E, (F) drill core F MS profile.

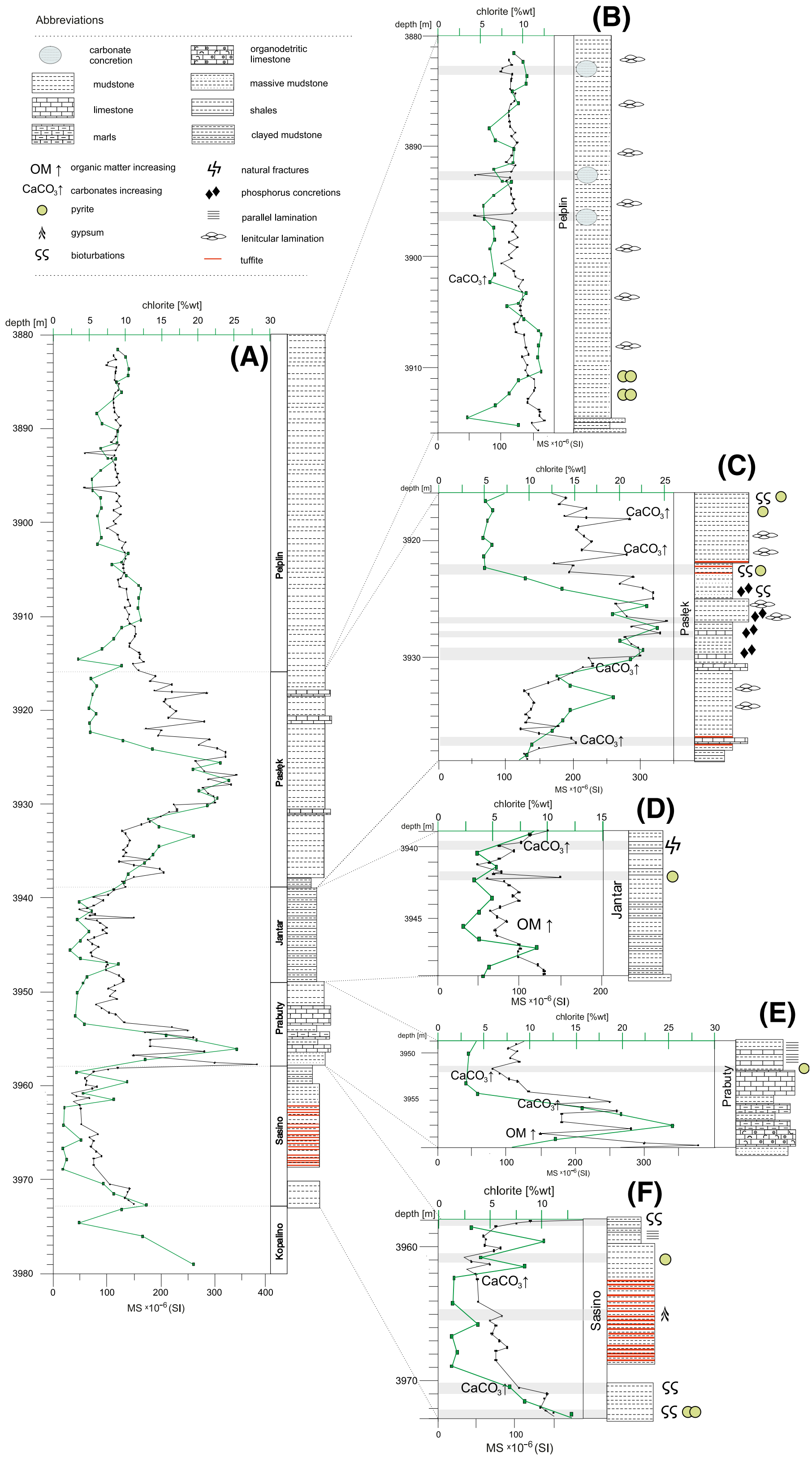

Figure 4. A comparison between magnetic susceptibility (MS) (black line) and the chlorite content (green line) through a lithological profile of drill core F, simplified (A) and more detailed, separated for each formation: the Pelplin (B), the Pasłęk (C), the Jantar (D), the Prabuty (E), and the Sasino (F). In gray, anomalies of MS are marked. OM = organic matter.

start to appear. This is the characteristic closure of the Pasłęk Formation in all the examined drill cores. Two positive peaks in this decreasing shape of the curve occur within the carbonate layers. Their texture suggests it may be early diagenetic carbonate cementation of mudstones.

The top of the last bioturbated layer begins the Pelplin Formation (green claystones; Wenlockian age) that contains grayish-black to gray laminated calcareous mudstones with a lenticular fabric commonly with thin (millimeters) tuff laminas and small amounts of fine (millimeters in diameter) pyrite concretions. Distinctive in the profile are carbonate concretions reaching decimeters in diameter (Niezabitowska et al., 2019b). The MS curve in the whole formation is characterized by medium values and corresponds with the monotonous lithology. From the bottom of the formation, a slight decrease of the MS curve is noticeable, but generally, after several meters upward, the shape of the curve is straight and constant (Figures 4A, 5, 6). The only deviations in the curve shape correspond to negative peaks related to the mentioned carbonate concretions.

Correlation of MS Logs with Mineralogical and Geochemical Variation through the Profile

The MS logging was correlated with the results of Rock-Eval studies, such as *TOC* index and *OI* (Figures 5, 6; Figures S5, S6, supplementary material available as AAPG Datashare 131 at www.aapg.org/datashare), which may reflect the chemical conditions at the bottom of sedimentary basin (Słowakiewicz et al., 2015). Both indices, obtained as a result of OM pyrolysis, may help to estimate the quality of oxygenation conditions present during sediment deposition (e.g., Anderson et al., 1981; Langford and Blanc-Valleron, 1990; Peters et al., 2007). In detail, the *OI* provides an estimate of the amount of oxygen-containing compounds, a parameter that increases upon aerobic biological decay and which reflects the early stage of chemical and depositional conditions of compaction and further cementation of analyzed rocks (Słowakiewicz et al., 2015). Note that the values of *OI* > 80 were excluded from interpretation because they coincided with very low (<0.5 wt. %) *TOC* contents, thus too low of a denominator (Derkowski and Marynowski, 2016).

The rock magnetic studies performed on the samples collected from the drill cores show that MS is mainly controlled by paramagnetic minerals (Niezabitowska et al., 2019b). Therefore, we assumed that changes of MS may be dependent on variable amounts of phyllosilicates throughout the profile, and we compared the MS curve with the natural gamma-ray logging profile (Figure 5; Figures S5, S6, S7, supplementary material available as AAPG Datashare 131 at www.aapg.org/datashare), which generally shows the percentage contribution of clays in the analyzed rocks. Both curves have negative relation in the lower part of the profile (the Sasino, Prabuty, and Jantar Formations), where large lithological changes are present, such as variable amounts of carbonates and transitions from bitumen claystones to marls and limestones. In the upper part of the profile (the Pasłęk and Pelplin Formations), no correlation was observed. In this interval, the natural gamma-ray curve shows low values and no significant variation. In turn, on the MS curves, we observed repeatable trends in all of the drill cores. Despite negative correlation between the total amount of phyllosilicates and MS, we observed a significant relationship between the MS curves and the percent amount of chlorites in the analyzed rocks (from XRD studies), also in the upper part of the profile (Figures 4–7; Figures S5, S6, supplementary material available as AAPG Datashare 131 at www.aapg.org/datashare).

Their original character and connections to the paleoenvironment confirm the observations of the sedimentological structures, such as variations of BI, which is also an oxygen condition index in itself. The most important observation is a positive correlation between MS, BI, and *OI* and a negative correlation with *TOC* index. The *TOC* parameter has a negative correlation with MS, which is noticeable for each formation. This observation is well visible in homogenous Jantar Formation, where DC is equal to 0.82 for the linear fit. In turn, for the Sasino Formation, characterized by carbonate inputs, DC is equal to 0.51 for power fit. Similarly, positive correlation between *OI* and MS differs between the formations; in this paper, the best correlation was found for more homogenous facies, like the Pelplin or Jantar Formation (DC = 0.71 and 0.63 for linear fit, respectively), whereas in more variable facies like the

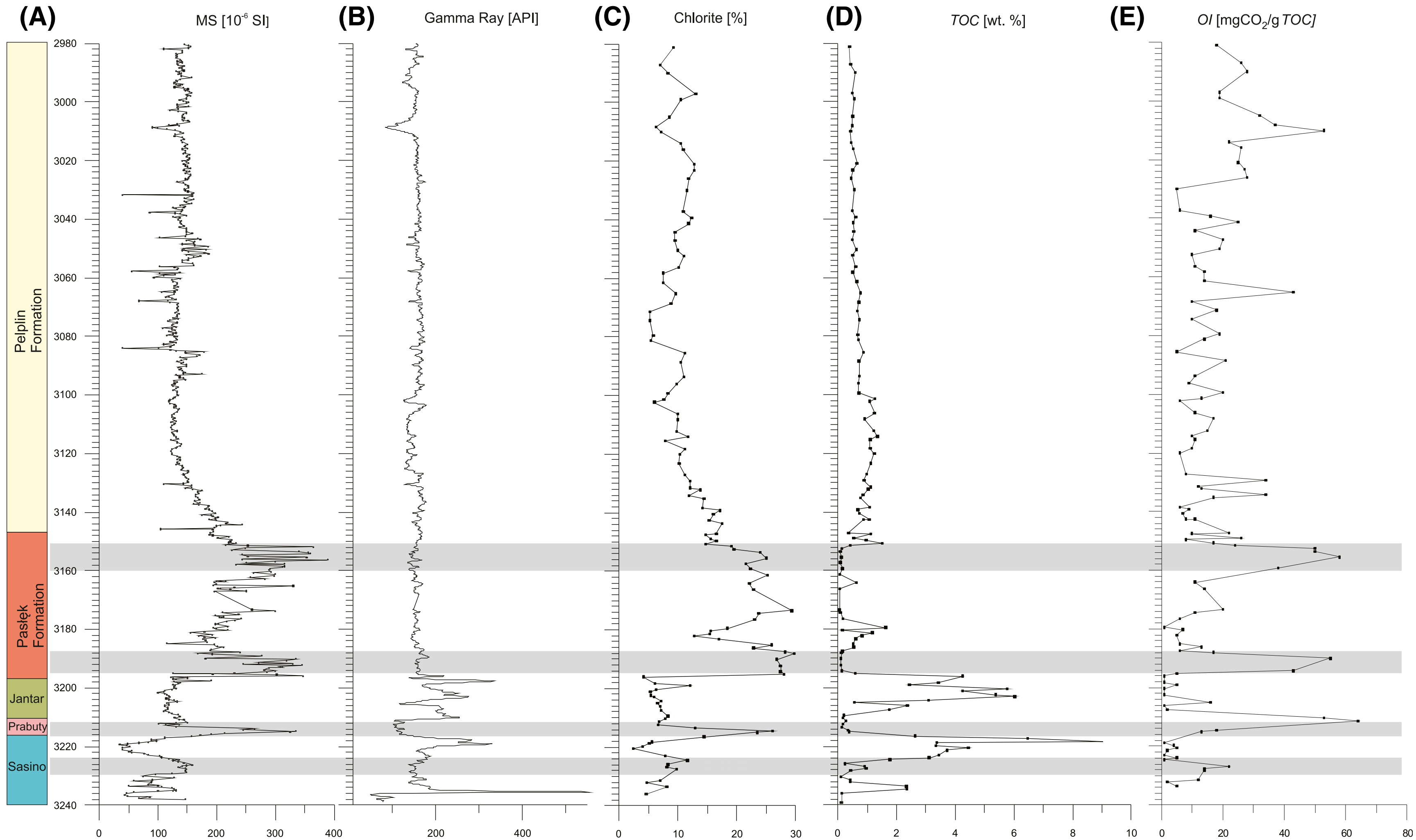

Figure 5. Vertical magnetic susceptibility (MS) log (A) from the Baltic Basin, displaying a succession from the Ordovician–Silurian rocks of drill core C. The MS profile is compared with the natural gamma-ray wire-line logging profile (B), the percent amount of chlorite (C), total organic carbon (*TOC*) content, (D) and oxygen index (*OI*) log (E). In gray, the characteristic peaks were marked to clarify differences in trends for each parameter.

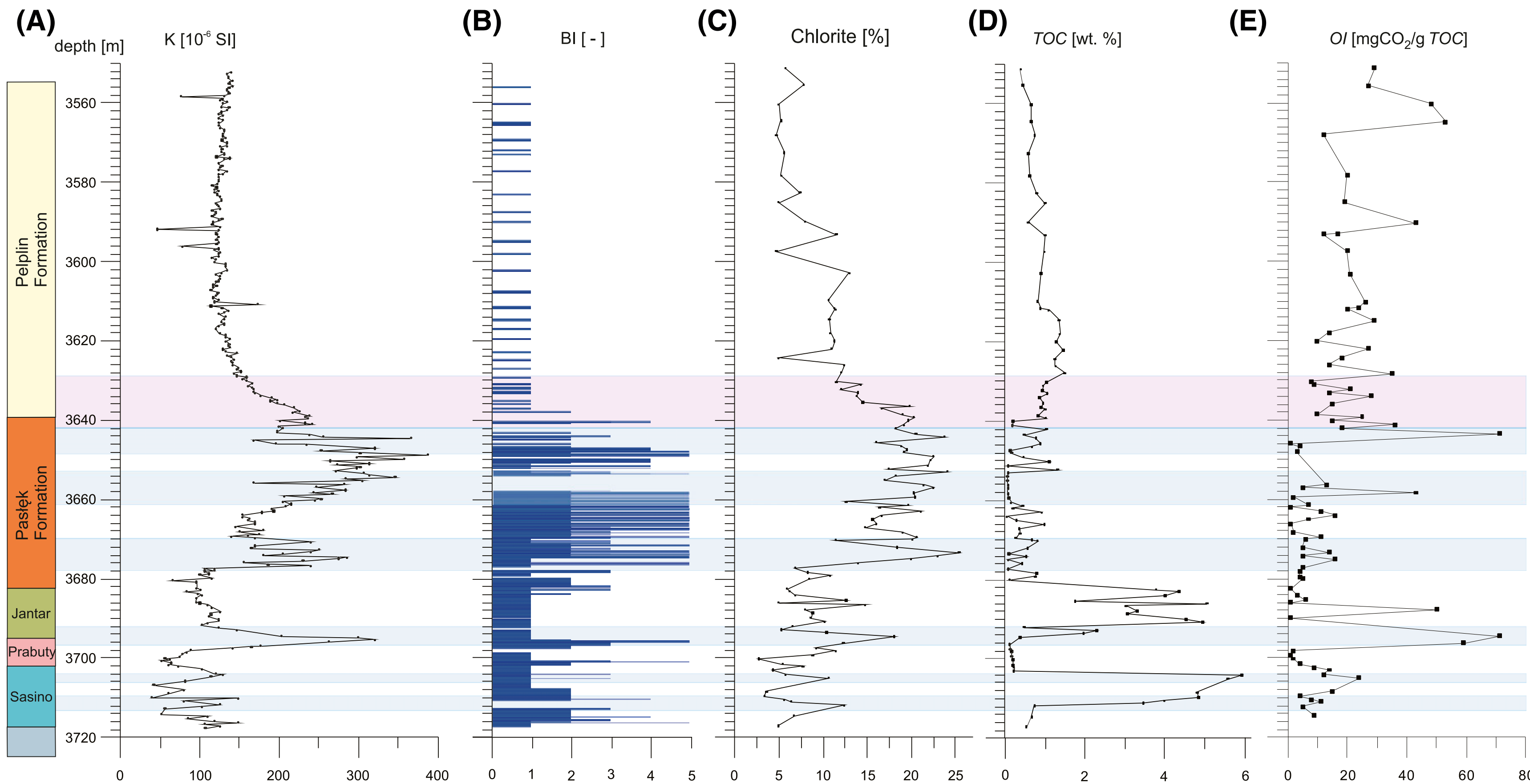

Figure 6. A detailed core log profile of magnetic susceptibility (MS) (A) from the Baltic Basin displaying a succession from the Ordovician–Silurian rocks of the drill core D. The MS profile is compared with the bioturbation index (BI) log (B), total organic carbon (*TOC*) content (C), oxygen index (*OI*) log (D), and percent amounts of chlorite (E). In gray and pink, characteristic peaks were marked to clarify differences in trend for each parameter. K = bulk magnetic susceptibility.

Sasino Formation, DC is equal to 0.55 for linear fit. In turn, for BI, positive correlation with MS is observable for the whole profile with DC equal to 0.82 for linear fit. These relationships suggest that the very early depositional or diagenetic conditions, including oxygen level at a bottom part of the basin (directly related to the BI and *OI*), might have influenced the origin and variations of MS throughout the lithological profile. This conclusion—together with the previously observed relationship between MS and chorite's quantity—has led to the conclusion that Fe occurring now in chlorite must have been present already during deposition or the early diagenesis stage (see the Discussion section for further argumentation).

A detailed comparison between the MS log and percent amount of selected minerals assumed that minerals containing Fe (e.g., dolomite, chlorite, mica) show the best correlation with MS (Figure 7). Note that the phyllosilicate curve (dark green line) arises from the sum of mica (purple line) and chlorite contents (light green). In turn, dolomite or Fe oxide has no significant variations, which may correlate with the MS changes, excluding single episodes of significant increases of dolomite amount (see example at a depth above 2890 m, Figure 7). Other minerals such as ankerite and pyrite also do not show a clear correlation with MS (Figure S7, supplementary material available as AAPG Datashare 131 at www.aapg.org/datashare).

Geochemical Relations

The results of XRD analyses show that general mineralogical composition of analyzed formations includes approximately 50% of phyllosilicates (up to 67% in the Pasłęk Formation, including up to 25% of chlorites), 20%–25% of quartz (with maximum 50% in the Sasino Formation), up to 10% of pyrite, and 7% of plagioclase. Calcium content does not exceed 12%; however, in layers enriched in carbonates or in concretions, 40%–50% content is reached.

The paramagnetic minerals, represented mostly by phyllosilicates (chlorite, illite) and pyrite, are dominant through the studied section. The highest pyrite contents were detected in two lowermost layers, Sasino and Jantar Formations, whereas chlorite and other phyllosilicates dominate the Pasłęk Formation. Moreover, layers enriched (up to 20%) in ferroan dolomite occur as well. Low-coercivity minerals (most likely magnetite, see Niezabitowska et al., 2019a, b) are present in all formations. The highest amounts of this mineral are observed in two lowermost formations, Jantar and Sasino. In turn, high-coercivity mineral, probably hematite (Niezabitowska et al., 2019a), is present in two uppermost formations, Pelplin and Pasłęk. Constant through the profile is diamagnetic quartz content, and occasionally significant content of calcite (up to 50%) slightly decreases MS values.

To obtain the Fe contribution from chlorite, a calculation procedure was applied, which subtracted Fe content from pyrite and the carbonates, based on these minerals concentrations measured with XRD from the total Fe concentration in bulk samples, labeled as method 1. This Fe content, likely contributed by chlorite as the only remaining Fe-bearing phase, forms a common trend with chlorite content measured with XRD (Figure 8A), implying that chlorite is indeed rich in Fe and the remaining bulk Fe fraction is from chlorite. If total bulk rock sulfur concentration is assumed as coming only from pyrite, the corresponding pyrite-Fe fraction can be subtracted from bulk Fe (method 2), and the remaining Fe fraction corresponds to Fe coming from chlorite and a substitution in carbonates. A high correlation of 1:1 between Fe fractions calculated with these two methods ensures correctness of the calculation and implies that carbonate contribution to bulk Fe is minimal. Calculated Fe content in chlorite reaches a maximum of ~30 wt. %, which corresponds to the Fe-rich chlorite reported by Topór et al., (2017).

DISCUSSION

Relationships between MS and Mineral Composition

The studied rocks represent a continuous stratigraphic profile (excluding the unconformity between the Ordovician and Silurian) from Upper Ordovician to upper Silurian and are characterized by various MS values. Our main observation is a lack of expected correlation between MS and natural gamma-ray logs but a good correlation between the percent amount of chlorites and MS (compare Figures 4, 7). These observations may be explained by a dependence of

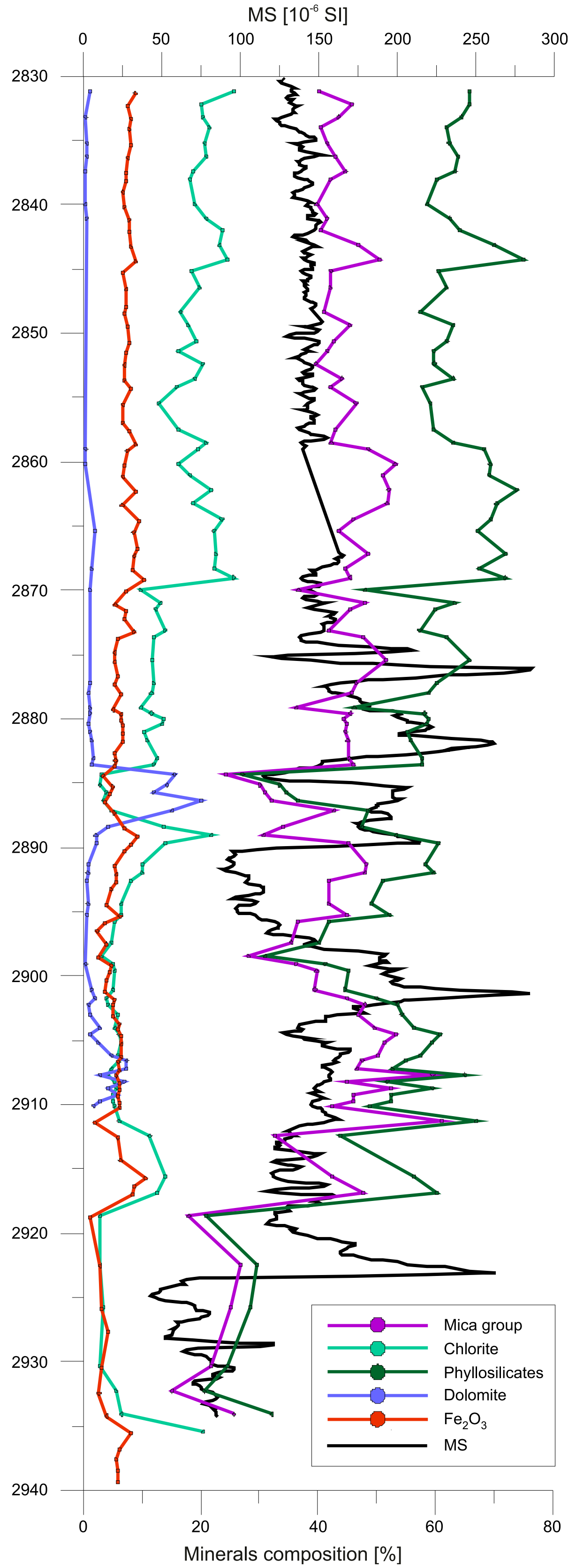

Figure 7. Magnetic susceptibility (MS) vertical variation in drill core A compared with the contents of selected minerals: chlorite and the mica group, the sum of all phyllosilicates, dolomite, and iron oxide.

natural gamma-ray logging on the amount of all the phyllosilicates in the rock. In turn, MS values are based only on those phyllosilicates that are characterized by the highest range of MS (containing higher amounts of Fe, sensu stricto). In the analyzed rocks, mostly chlorite and illite are observed. Low-field MS values are equal to 5×10^{-4} SI for chlorite and 410×10^{-6} SI for illite (e.g., Hunt et al., 1995; Martín-Hernández and Hirt, 2003).

However, we cannot exclude that MS in the lower part of the profile is also influenced by other paramagnetic minerals, such as ankerite, ferroan dolomite, or pyrite. Detailed analysis of MS variation shows that specific characteristic peaks connected to the "deposition sedimentary events" accompany the general shape of the MS curve. They are associated with the local increasing contents of pyrite, phosphate concretions, or different kind of carbonate minerals. Layers associated with these "events" sometimes are only several centimeters in thickness and so may not be visible on mineralogical logs.

Nevertheless, we did not observe any clear correlation between the percent amount of dolomite and MS values in the available interval (Figure 6), neither between MS nor the percent amount of pyrite (Figure S7, supplementary material available as AAPG Datashare 131 at www.aapg.org/datashare). However, high pyrite contents were observed in the highest Fe content samples (Topór et al., 2017). Interestingly, even significant amounts of pyrite (greater percentages in the Jantar Formation), which MS values range between 35 and 5000×10^{-6} SI (after Hunt et al., 1995), generally do not significantly influence the shape of the MS curve (Figure S4, supplementary material available as AAPG Datashare 131 at www.aapg.org/datashare). This fact might arise because of significantly higher values of MS for Fe-chlorite, which is present in amounts similar to pyrite.

A noticeable influence of diamagnetic minerals enriched in calcium carbonate was also observed, for example, in the upper part of the analyzed interval, in the Pelplin Formation. Despite this facies being reasonably well oxygenated during deposition (low *TOC* content [<1.3 wt. %], BI = 1, calcium carbonate input), the amount of chlorite and values of MS decrease and stay low (between 5% and 10% and slightly above 100×10^{-6} SI, see Figures 4, 6). This phenomenon may be explained by the general increase of calcium carbonate content in the whole interval, caused by strong input of eastward carbonate platforms, at the expense of reduced delivery of detrital material.

Paleoenvironment

Crucial for further paleoenvironmental interpretation is to define what stage of rock formation did determine MS. We observe the positive relationship between MS alteration, percent amount of chlorite, *OI*, and BI variations, whereas for *TOC* it is negative. The relationship suggests that the values of MS were determined at a relatively early stage of rock formation, in which biological activity in oxygen-rich conditions was present. These specific conditions are gained by high values of two parameters, the *OI* and BI. Moreover, a negative correlation between *TOC* and MS suggests that the preservation of magnetic minerals, determining the MS value, takes place in the absence of OM.

Our results indicate that the amount of chlorite is responsible for MS variations. Therefore, defining the origin of this mineral assemblage is crucial in understanding the origin of MS variations. Chlorite in small amounts can have both detrital and diageneic origin; however, presence of chlorite abundant in sediments (in this study, even 25%) suggests its diagenetic origin (e.g., Hillier, 1978). Moreover, detrital chlorite in sediments is usually confined to high-latitude deposition (Chamley, 1989; Weaver, 1989). In turn, diagenetic origin can be associated with early diagenetic stage in shallow marine environments, where the 0.7-nm (7Å) mineral berthierine or odinite is formed in tropically weathered landscape highly supplied with colloidal Fe (Porrenga, 1967; Bailey, 1988; Odin, 1988). Further, this synsedimentary Fe-rich mineral usually alters into Fe-rich chlorite during burial diagenesis (e.g., Hillier, 1978; Velde, 1989). Considering the presence of highly illitized illite–smectite mineral in the rocks studied, which is the evidence for another important reaction typical for shales deep diagenesis, the diagenetic origin of Fe-chlorite is highly probable (e.g., Hower et al., 1976; Ahn and Peacor, 1985; Weaver, 1989; Compton, 1991; Scasso and Kiessling, 2001; Wilson et al., 2016). The authigenic origin of chlorite in analyzed rocks should be expected because they are affected by burial conditions at temperatures above 80°C (Grotek, 1999; Środoń and Clauer, 2001). This is consistent with the studies of Topór et al. (2017), who found the relation between chlorite content increasing with depth to a maximum of 33 vol. % close to the Teisseyre–Tornquist zone (see Figure 1), which reflects the progression of burial diagenesis.

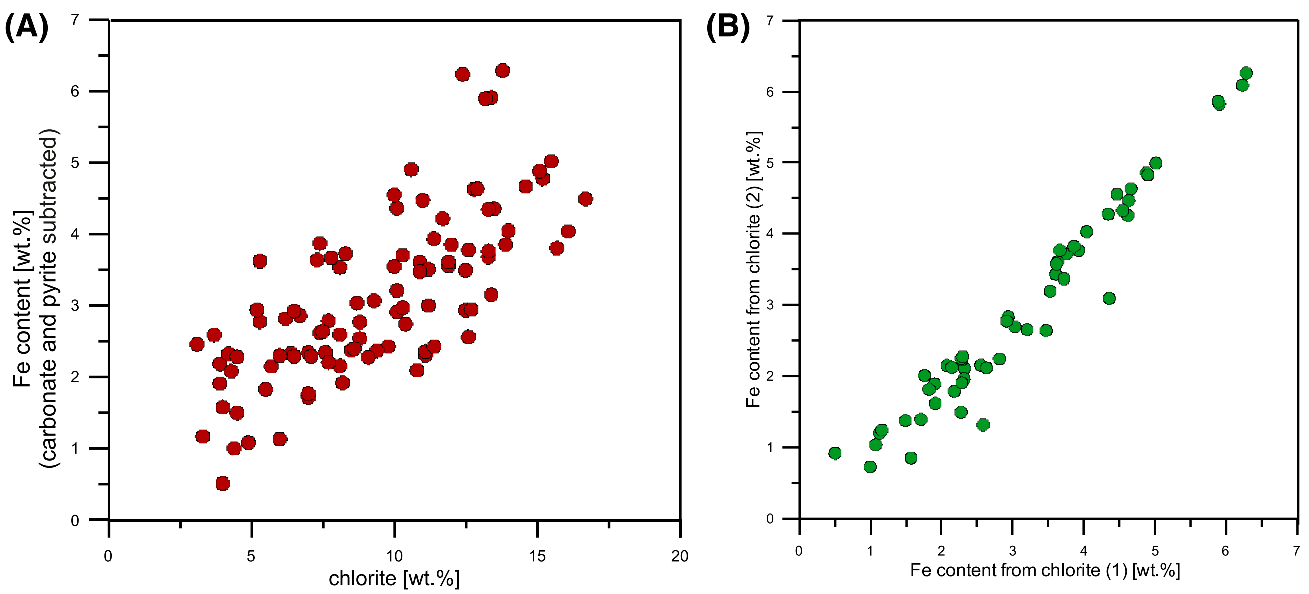

Figure 8. The relationship of Fe-chlorite with Fe content (A) and comparison between Fe content in chlorite calculated by two methods (B). Scattered trend in (B) comes from precision limit in chlorite determination with x-ray diffraction (~2%).

Nevertheless, likely deep diagenetic origin of chlorite does not explain the source of Fe-rich clay minerals constituting substrates to form ferroan chlorite during further diagenesis. Therefore, based on the studies of Odin (1988), Bailey (1988), and Aagaard et al. (2000), we suggest early diagenetic formation of ferric synsedimentary Fe-rich clays as precursors for Fe-chlorite modification. This is consistent with the subtropical environment conditions during sediment deposition in shallow marine deposition systems (e.g., Calner, 2005; Kiipli et al., 2012).

The oxygen level, which determines preservation of OM, is crucial when considering the deposition of rocks containing Fe supplied from land, which confirms studies of ironstone deposits and experimental data (e.g., Odin, 1988). In such conditions, the precipitation of these minerals arises from concentration of deposits from land, Fe, and oxygenated conditions in the sediment, which appear in the absence of OM (Odin, 1988; Harder, 1989; McKay et al., 1995). This process is consistent with our observation of a negative correlation between the percent amount of chlorite and *TOC* (Figures 5, 6).

Summarizing, our findings suggest that the very early stage of rock formation determines values of MS. Important factors controlling MS variation are oxygen conditions in the seabed and a related amount of OM. Generally, high MS values (above 200×10^{-6} SI) are supported by highly oxygenated conditions during sedimentation that implicates a low amount of preserved OM. The composition of minerals and rocks delivered from land (including Fe-bearing minerals) is modified within further diagenesis. However, the element content is stable in this closed system (Tarling, 1999). In general, Fe occurrence in the sedimentary basin will be part of pyrite- or Fe-rich phyllosilicates, depending on oxygen conditions. Considering the supply of detrital material, it is also worth highlighting the sedimentation rate, which may also determine the amount of ferroan clays and thus the amount of diagenetic Fe-chlorite. Generally, higher values of MS may be related to the increase of detrital input. In a regional context, the amount of chlorite may be linked to changeable relief resulting from the Caledonian orogeny, associated with more widespread exposure of chlorite-rich (low-grade) metamorphic rocks, and stripping off more mature soils (after Hillier, 1978). However, this complex issue needs further investigation, including calculation of statistical parameters describing observed relationships.

CONCLUSIONS

The MS logs reveal a similar pattern in all analyzed drill cores from northern Poland across the Baltic Basin. We observed lower values of MS in the Sasino and Jantar Formations (enriched in OM), medium values in the Pelplin Formation, and the highest values in the Pasłęk and Prabuty Formations (internally diverse and enriched in calcium carbonates).

We observe a positive relationship between MS variation and percent amount of chlorites throughout the profiles, linked to the lithology. Moreover, we found localized events: (1) a rapid increase of MS values related to thin layers enriched in dolomite and phosphate concretions and (2) a decrease resulting from the enrichment of concretions or layers of calcium carbonates.

The good correlation between the MS curve with bioturbation and *OI* variation (indicative of biological activity) led us to the conclusion that the MS variation shows positive correlations with dissolved material in marine water oxygen at the very early stage of rock formation. Moreover, MS variation is also consistent with the amounts of chlorite through the profile. Thus, to understand the origin of MS variation, it is crucial to define the origin of the mineral. We interpret Fe-chlorite as a product of deep diagenesis, in which Fe-rich clays, precursors of chlorite, were modified by thermal alteration. In turn, chlorite precursors have early diagenetic origin because they occurred in a sedimentary basin as a ferric synsedimentary clays, while further diagenesis modified them to ferrous clays. During the initial deposition of sediments, the amount of substrates (ferroan clays) is defined by oxygen level at the bottom part of the sedimentary basin.

In summary, MS measurement is a relatively fast and cheap measurement tool for regional drill core correlations. It may be successfully used as a paleoenvironmental indicator. We propose the following interpretation of MS values: high values (above 200×10^{-6} SI) suggest highly oxygenated conditions during sedimentation of gas-bearing shales and thus the low amount of preserved OM. In turn, low MS values (below 100×10^{-6} SI) likely indicate depletion in the oxygenic environment and probably high content of OM.

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