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ORIGINAL PAPER

Geochemical history of a Lower Miocene lake, the Cypris Formation, Sokolov Basin, Czech Republic

Bohdan Kříbek · Ilja Knésl · Petr Rojík · Ivana Sýkorová · Karel Martínek

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Abstract The intracontinental Lower Miocene Cypris paleo-lake originated during progressive subsidence in the Sokolov Basin, part of the Cenozoic Ohře Rift, after the deposition of coal seams. The Cypris Fm. consists almost entirely of lacustrine clays with variable mineral composition and organic matter, where this succession is 70–120 m thick. The main objective of this study was to interpret the geochemical history of the Lower Miocene Cypris Fm. using high-resolution, down-core geochemical records and study of the organic matter. This work revealed that the lower part of the lacustrine sediment sequence was deposited in a freshwater lake, in an open hydrological system. An increase in the K/Zr and K/Ti ratios towards the upper part of the Cypris Fm. indicates a gradual increase in the pelitic fraction of the local sediments and/or a decline in input of volcanic material. Simultaneously, increasing Ca/K and Sr/K ratios indicate the precipitation of carbonates, predominantly dolomite and siderite. In the upper part of the Cypris Fm., there is a significant increase in Na/K, Na/Zr, and Na/Ti ratios, suggesting increasing salinity (alkalinity) of the paleoenvironment in a closed hydrological system. Reaction between the Na-rich water and clastic components of the sediment in an alkaline medium gave rise to the formation of zeolites, mixed-layer clay minerals and smectite. Abundant remains of aquatic organisms, especially algae, increased with greater salinity in the upper part of the Cypris Fm. This is reflected in the greater hydrogen index ($HI_{Rock\ Eval}$), and the growing proportion of liptinite group macerals of aquatic origin in the bulk organic matter. During the entire history of sedimentation in the Miocene lake, repetitive changes in the sediment geochemistry occurred at both micro- and macroscales, and fluctuations of K/Ti, K/Zr, and Sr/Ca ratios over meters to tens of meters are observed. These changes probably reflect either long-term climate fluctuations during the Lower Miocene or oscillations caused by changes in the rate of subsidence of the basin floor. Variations in the elemental composition of sediments can be used to correlate individual boreholes across the entire sedimentary basin.

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B. Kříbek (✉) · I. Knésl
Czech Geological Survey, Klárov 3, 118 21 Prague 1, Czechia
e-mail: bohdan.kribek@geology.cz

P. Rojík
Sokolovská uhelná, Ltd., Staré náměstí 69, 35 601 Sokolov, Czechia

I. Sýkorová
Institute of Rock Structure and Mechanics, Academy of Science of the Czech Republic, V Holešovičkách 41, 182 09 Prague 8, Czechia

K. Martínek
Faculty of Science, Charles University, Albertov 6, 128 43 Prague 2, Czechia

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Introduction

Reconstruction of Miocene marine paleoenvironments has received considerable attention because of the need to understand carbon cycling in oceans and to comprehend the extent and rate of warm to cold climate changes during the Miocene (Woodruff et al. 1981; Zachos et al. 2001). In contrast, studies of temporally equivalent continental records are limited. Intracontinental basins should, however, record climate conditions related to continental weathering and provide estimates of erosion rates and chemical budgets. Formation of numerous rift lakes such as Lake Baikal (Fagel et al. 2003), those in the African Rift Valley (Séranne 1999) and those in Western Europe (Renac et al. 2013a, b) and Central Europe (Matys Grygar and Mach 2013; Matys Grygar et al. 2014) began during the Oligocene to Miocene.

The initial continental Ohře (Eger) Graben (Czech Republic) hosts the Most, Sokolov and Cheb basins, which are filled with thick Paleogene to Pliocene siliciclastic sediments and coal seams (Fig. 1). In a broader context, the Ohře Graben is part of the European Cenozoic Rift System (Rajchl et al. 2009). In the pre-rift stage, the basin floors were affected mainly by Oligocene subsidence, volcanism and subsequent weathering, erosion and sedimentation in lake and swamp environments. The basin floor was later covered by extensive peat swamps that gave rise to coal seams. The overlying sediments of peat swamps are composed of claystones of the Cypris Fm. that were deposited in basin-wide lakes.

The main objective of this study was to interpret the geochemical history of the Lower Miocene Cypris Fm. using study of high-resolution, down-core geochemical records and organic matter. This included reconstruction of the sedimentary environments of the study interval in the central and marginal parts of the basin, and interpretation of the immediate controls (i.e. siliciclastic flux, lake metabolism), and the primary controls (i.e. climate changes, autocyclicity, episodic faulting) on the depositional stacking pattern of the lacustrine sediments. Changes in the chemical composition of the sediments were investigated using ratios of elements that enable identification and assessment of the sediment sources (Franz et al. 2006; Roy et al. 2008a, b), changes in the paleoenvironment of the studied lake basins and past climate conditions (Kylander et al. 2013; Matys Grygar and Mach 2013; Matys Grygar et al. 2014; Wennrich et al. 2014; Jin et al. 2015).

Chemical changes in the organic composition of the sediments were compared with the evolution of organic matter that forms an essential part of the Cypris Fm. claystones. Inorganic and organic components of the sediment were studied to assess the possibility of their use in correlation of boreholes drilled at multiple sites across the Sokolov Basin.

Geologic setting of the Sokolov Basin

The Sokolov Basin (SB) is a continental Tertiary basin that extends in a WSW-ENE direction and intersects the Hercynian basement of the Bohemian Massif (Fig. 1). Discontinuous Cenozoic fill reaches a maximum thickness of 360 m. Most of the basin margin deposits were eroded and what remains of the sediment record is represented mainly by deposits preserved in the central part of the basin. Peak tectonic, volcanic and sedimentary activities occurred during the Oligocene and Miocene, forming narrow depressions in an E-W direction. The fill of the SB was divided by Rojík et al. (2014) into four tectonosedimentary and lithostratigraphic units. The Staré Sedlo Fm. (Upper Eocene to Lower Oligocene) consists of sands, sandstones, gravels and conglomerates interbedded with lenses of silty kaolinite clays. The sediments were deposited in shallow depressions into which short rivers flowed from all directions.

The Nové Sedlo Fm. (Upper Eocene; Fig. 2) is composed of effusive and volcaniclastic rocks and marks the first major stage of extension of the SB related to intensive tectonic movements and volcanic activity. Subsidence of the basin floor and volcanism were synchronous (Rajchl et al. 2009).

The Miocene Sokolov Fm. (Eggenburgian to lowermost Ottangian; Fig. 2) reflects the second period of intensive basin expansion associated with volcanism and subsidence of the basin basement. Effusive, volcaniclastic and sedimentary rocks of the Sokolov Fm. were deposited in various environments (volcanic, lahars, gravitational streams, fluvial and peat-bogs). In

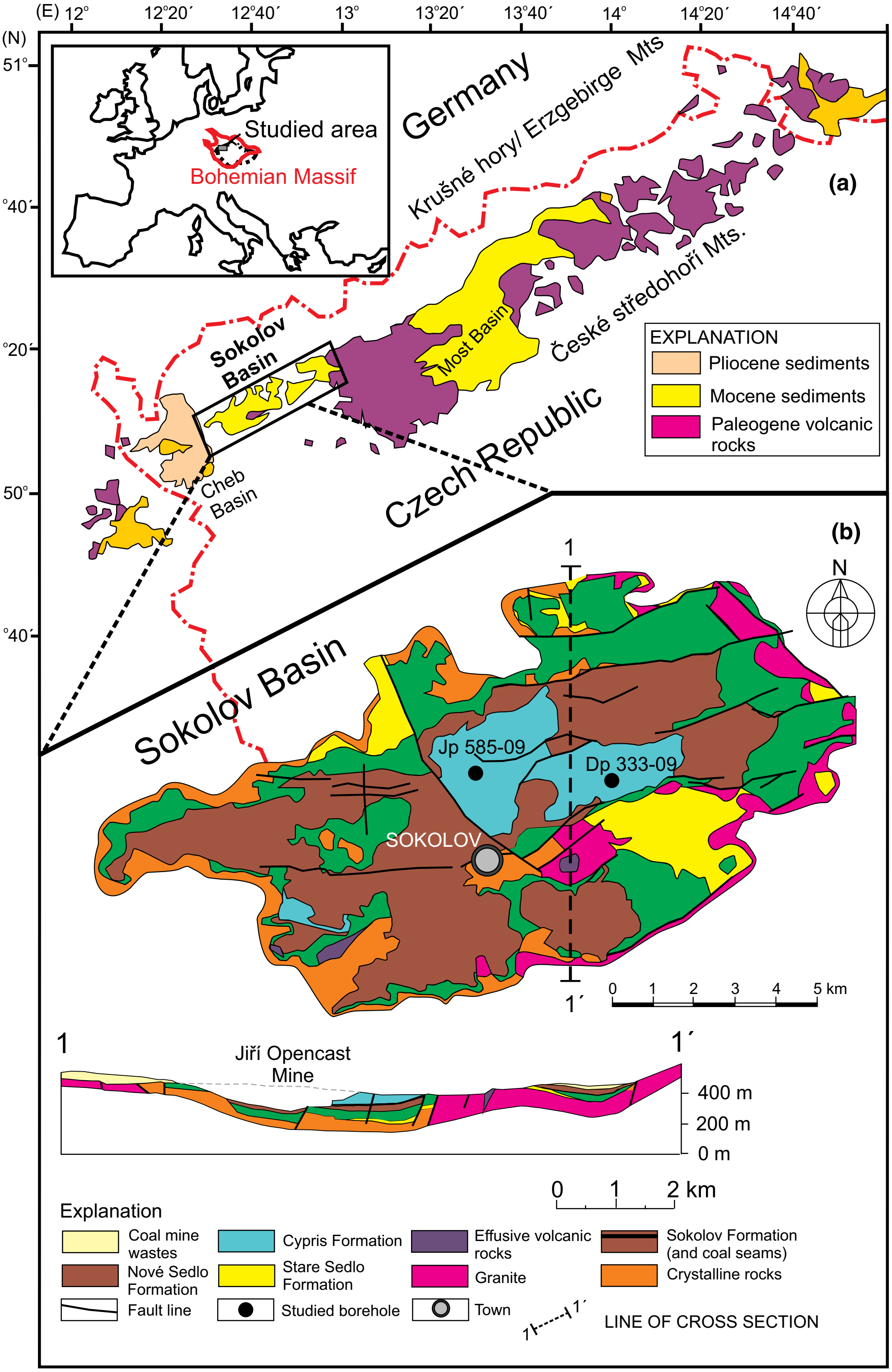


Fig. 1 **a** Geological sketch map of the Ohře Graben [A; modified after Matys Grygar and Mach (2013)], and a detailed map of the Sokolov Basin [after Rojík et al. (2014)] with locations of the studied boreholes (**b**)

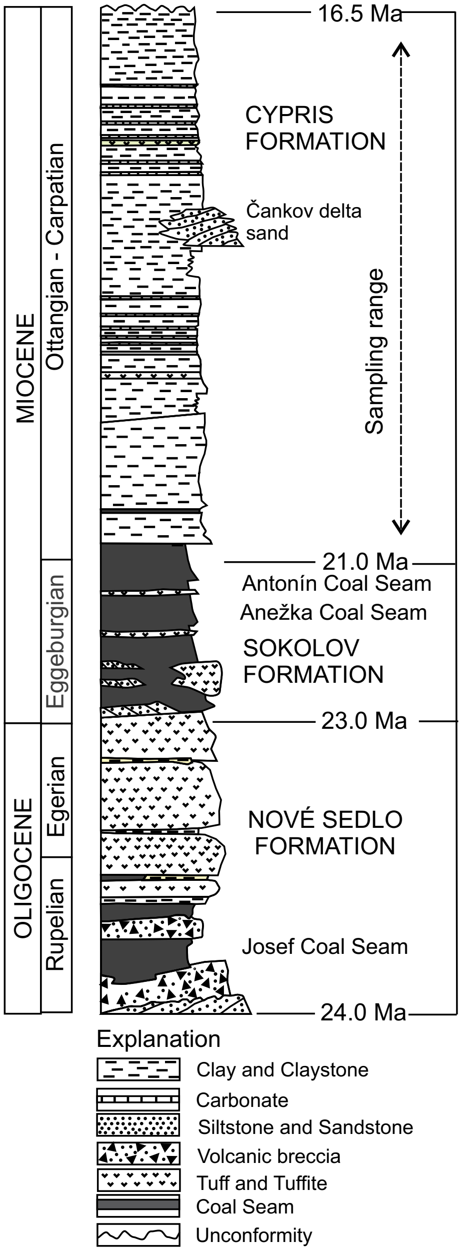


Fig. 2 Stratigraphic scheme of the Upper Oligocene to Miocene part of the Sokolov Basin fill, after Rojík et al. (2014)

the past, subbituminous coal was mined in numerous opencast mines and, to a lesser extent, also in underground mines. At present, only the Jiří Opencast Mine is active, with production of 6.3 Mt a year.

The studied sediments of the lacustrine Cypris Fm. (Ottangian to Karpathian; Fig. 2) form the roof of the exploited coal seams (Dopita et al. 1985) and attain a thickness of up to 182 m in the central part of the SB. The boundary between the coal seams and the overlying Cypris Fm. is sharp and indicates a sudden change in the tectonic regime, subsidence of the basin bottom or uplift of tectonic blocks that form the boundary of the basin area.

Published data on faunal and floral assemblages place the lower part of the Cypris Formation in the Ottnangian to Carpathian (Burdigalian; Fejfar 1989). Three relatively thin intervals of normal magnetic polarity were recognized in the Cypris Fm. in two correlated boreholes. The base of the Cypris Fm. is correlated to the lower part of normal-polarity chron C5En or the upper part of the underlying reverse-polarity chron (ca. 18.4 Ma). The normal-polarity chron identified in the upper part of the Cypris Fm. was interpreted as the Burdigalian chron C5Dn (16.7 Ma; Kadlec et al. 2011). The unit consists predominantly of massive or laminated claystones. Kaolinite is the major mineral in the lower part of the Cypris Fm. Upward, illite and sericite are more widespread and eventually become dominant. Smectite group minerals occur in variable amounts, and chlorite or biotite may also be present in the uppermost part of this formation. The claystones contain finely dispersed coal- or algae-type organic matter. Organic carbon content in the sediments ranges between 1.8 and 6.8 wt%, although it can reach 18 wt% in thin layers of organic matter-rich claystones (Kříbek et al. 1998). Sediments of the Cypris Fm. contain strongly fluorescent alginite (Type I kerogen), some sporinite, bituminite, and sporadic huminite (textinite) and inertinite (<5 vol%; Kříbek et al. 1998). Off-line pyrolysis spectra of organic matter consist mainly of alkanes and the corresponding 1-alkenes. The H/C atomic ratio of bulk demineralized organic matter is 1.56–1.62, and the high Rock–Eval HI values range from 594 to 653 mg HC/g TOC. Relatively high content of pentacyclic triterpanes of the hopane series suggests the occurrence of algae (*Botryococcus*, Kvaček et al. 1987) as primary producers. The claystones are light brown in color and contain the shells of ostracods, clusters of fish scales and bones, siliceous gastrolites and nodules of pyrite, greigite, smythite and pyrrhotite. A typical feature of the Cypris Fm. is an admixture of carbonates, mainly siderite, calcite, dolomite and ankerite. Several tuffaceous horizons are present in the Cypris Fm. In fact, redeposited volcanic material is present throughout almost the entire Cypris Fm.

Periods of sediment deposition in freshwater in the lake alternated with periods of increased salinity (Kvaček et al. 1987). Higher salinity is indicated by the occurrence of gypsum in the lacustrine sediments, and is supported by study of sulfur and oxygen isotopes (Šmejkal 1978). In the late stage of the Cypris Fm. evolution, the sedimentation environment changed from one of a permanent lake to one of intermittent lakes. According to Rojík et al. (2014), insufficient mixing of heavier brine at the bottom of the sedimentation basin resulted in meromixis, marked by permanent water-column stratification. Evidence that anoxic conditions affected the lake bottom is found in the occurrence of framboidal Fe-sulfides (greigite), the absence of ichnofossils and the preservation of sediment laminations. Uppermost, oxygenated waters became episodically eutrophic, as documented by the accumulation of fossil remains on bedding surfaces (oryctocoenoses) across the whole area of the depression. During arid seasons, large areas of these lakes dried out, leading to the formation of carbonate duricrusts with desiccation cracks (Rojík et al. 2014).

Materials and methods

Sampling

Samples were collected from two drill cores taken by Sokolovská Uhelná Ltd. in 2009 and 2010. Borehole Dp 333-09 was located in the peripheral area of the Sokolov Basin and borehole Jp 585-09 was in the central part of the basin (Fig. 1b). Maximum thickness of the Cypris Fm. in borehole Dp 333-09 was 74.8 m, whereas in borehole Jp 585-09 it reached 94.3 m. Samples from boreholes were taken at 10-cm intervals. Additional samples of Cypris Fm. sediments were taken from the walls of the abandoned Medard and Marie opencast mines. Samples of weathered crystalline rocks (including china clay), volcaniclastics and bentonites were taken from outcrops in several opencast mines to measure chemical composition and determine possible sources of the sediment.

Mineralogy

The mineralogy of collected samples was studied using a Philips X'Pert System diffractometer, CuKα, 40 kV/40 mA, equipped with a secondary graphitic monochromator. Records of non-oriented samples of the Cypris Fm. claystones (range 3°–70° 2θ, increments of 0.05 2θ, 3 s) were collected, as were records of the oriented preparation of the claystone fraction, before and after saturation with ethylene glycol (range 2–50° 2θ, increments of 0.05 2θ, 2 s). Separation of the <2-µm fraction was performed at the Czech Geological Survey branch in Brno using sedimentation in distilled water, and was thickened by centrifugation. Claystone fractions were used to make oriented preparations by suspension sedimentation on a slide.

X-ray diffraction records of oriented preparations of separated claystone fractions were loaded in the natural state after saturation by ethylene glycol. The structure and expandability of the mixed-layer illite/smectite were determined by record comparison with a simulation of mixed-layer illite/smectite with various expandabilities using the NEWMOD program.

The claystone mineralogy and surface distribution of elements in the rocks were studied with a CAMSCAN electron microscope equipped with a LINK-ISIS energy-dispersive X-ray analyzer (Oxford Instruments). The acceleration potential was 15 kV and the emission current was 3×10^{-9} A.

Inorganic geochemistry

The distribution of selected chemical elements in rocks was determined using a portable X-ray fluorescence analyzer (PXRF, spectrometer Alpha, Innov-X, Woburn, USA), calibrated using internal and external standards. Rock samples were dried and crushed to <2 mm in size. In total, 1635 samples were analyzed. To verify results, selected control samples were analyzed in the Canadian ACME laboratory accredited under ISO 9002, after complete rock dissolution by an acid mixture (including HF) using the ICP-MS method. The relative percent difference (RPD) using CRM OREAS 25a, and OREAS 45e for most of the chemical elements was excellent (±10% of the certified values) or good (±10–25%). In total, 90 samples were analyzed. There was very good agreement between concentrations of most elements analyzed by PXRF and by ICP-MS in Canada. Comparison of concentrations established by the two methods is shown for Zr and As in Fig. S1. Because concentrations of Si and Na cannot be determined using PXRF, they were established by atomic absorption spectroscopy (AAS) in the accredited laboratory of the Czech Geological Survey.

Organic petrography

Maceral analyses of the huminite, liptinite, inertinite groups and measurements of the random reflectance of huminite as a rank parameter (Taylor et al. 1998; ICCP 2001; Sýkorová et al. 2005) were carried out on a set of samples from the Cypris Fm.

Polished sections were prepared for petrographic analyses and studied both in reflected and ultraviolet light using an Olympus BX51 microscope with Zeiss Photomultiplier MK3 system and fluorescence mode using an immersion lens with 40× magnification. The Pelcon point counter was used for maceral analysis. Random and actual reflectance values were determined from polished sections by SpectraVision software calibrated with spinel ($R = 0.422\%$), sapphire ($R = 0.596\%$) and yttrium aluminum garnet ($R = 0.894\%$) standards.

Rock–Eval type analyses were carried out using a ROCK EVAL 5 instrument. Nitrogen was used as the carrier gas. The analytical cycle began with measuring the initial isotherm for 5 min at 250 °C, and finished at a temperature of 650 °C, attained at a constant heating rate of 25 °C/min. The contents of organic and mineral carbon were determined on an ELTRA CS 1000 S instrument.

Data analysis

Summary statistics of the analytical data set were first calculated to evaluate distributions. The frequency distribution for each set of elements was examined using histograms, Q–Q and P–P diagrams. Kurtosis and skewness were calculated using the S-Plus program version 4.5 (MathSoft Inc., Seattle, WA, USA, 1997). Because the statistical distribution of most variables determined by chemical analyses was not normal, non-parametric methods were used to assess the main statistical characteristics of the individual data populations, again using the S-Plus program version 4.5. For statistical treatment, chemical concentration values below the detection limit were replaced by values equal to 1/2 of the detection limit.

Principal component and cluster analyses were performed using the Statistica software, version 10.0 MR1 (StatSoft, Inc. Tulsa, USA).

Results

Lithology of Cypris Formation claystones

Because the vast majority of the Cypris Fm. is composed of claystones and siltstones with variable contents of carbonates and organic matter, attention was focused on these rocks. Results confirmed that the lithology of the lower and upper parts of the Cypris Fm. differs considerably.

Claystones and siltstones, usually without apparent laminations, predominate in the lower part of the Cypris Fm boreholes. They consist mainly of clay minerals, quartz, finely dispersed organic matter and larger clasts of coal with irregular boundaries. A roughly 40-cm-thick coaly siltstone bed (“coal stringer”) occurs in the lower part of the formation. Laminated claystones are minor. Laminations are composed of alternating tiny beds that are relatively richer or poorer in organic matter. Laminae that are rich in organic carbon at the bottom of both studied boreholes are discontinuous, and their thickness does not exceed several microns (Fig. S2a). Carbonates are usually dispersed in the clayey matrix of sediments (Fig. S2b). The major minerals include quartz (11–12 vol%), siderite and dolomite (11–16 vol%), kaolinite and K-feldspar. Minor minerals are represented by anatase, muscovite/illite, calcite (1–5 vol%) and ankerite (0–5 vol%), whereas zeolites are accessory minerals. Pyrite is present in the form of both euhedral grains and framboids.

Kaolinite in the clay fraction of the sediments strongly predominates over illite and the mixed-layer mica-clay minerals of the illite–smectite group ($K \gg M > \sim I/S$), in which the expandability of these minerals is low, and does not exceed 30% of the smectite. Smectite as a separate mineral is rare.

Laminated claystones predominate over claystones without distinct laminations in the upper part of the Cypris Fm. Laminae that are rich in organic matter, in comparison with those in the lower part of the formation, are continuous on a microscopic scale and their thickness is substantial (tens to hundreds of micrometers; Figs. S2c, S3a, b). The amount of quartz varies between 10 and 14 vol%, and the content of carbonates (dolomite and siderite) is also significantly greater compared with the lower part of the formation (5–26 vol%). Claystones of the upper part of the Cypris Fm. contain numerous layers of laminated or non-laminated clay ironstones or clayey dolomites with high iron content the thickness of which attains a maximum of 30 cm. Compared to the lower part of the formation, the amount of analcime $NaAlSi_2O_6$ H_2O is much greater and becomes a major component in certain layers (Figs. 3, S4). Potassium feldspar in the form of clastic grains is a common mineral whose alteration is manifested by reduced potassium content in the peripheral parts of the grains (Fig. S3c). Gypsum is an accessory mineral. Mixed layer mica-clay minerals of the illite/smectite group and smectite prevail over kaolinite, illite and detrital muscovite in the upper part of the Cypris Fm. The expandability of the mixed layer clay minerals is significantly higher than in the lower part of the formation (40–60% S). The amount of minerals with the I/S mixed-layer structure is estimated to be 24–27 vol%, that of kaolinite 12–25 vol%, and that of illite 2–11 vol%. Pyrite is a common mineral in the upper part of the Cypris Fm. Amounts of X-ray amorphous phases such as organic matter and amorphous forms of quartz in the upper part of the formation range from 5 to 30 vol%.

Macerals of the Cypris Fm. claystones are of terrestrial or aquatic origin (Table 1).

The terrestrial macerals include those of the huminite group (textinite, ulminite and gelinite; Fig. S5a), inertinite group (fusinite, semifusinite, macrinite and inertodetrinite), and liptinite group (resinite, sporinite, cutinite and suberinite). The terrestrial macerals are randomly dispersed throughout most claystone samples in low abundances, typically lower than 5 vol%, and they are commonly 10–50 µm in size. The amount of huminite and inertinite-group macerals, however, is high (15.7–26.8 vol%) in the thin layer of coaly claystone ("coal stringer") in the lower part of the Cypris Fm.

Ulminite, textinite and gelinite particles exhibit well-defined boundaries and demonstrate random reflectance between 0.15 and 0.26%, which corresponds to a low degree of coalification (ortho-lignite; ECE-UN 1998). Inertinite particles (fusinite, semifusinite, macrinite) are present in nearly all the samples. Particles of sporinite and resinite prevail in the liptinite group macerals of terrestrial origin (Fig. S5b), while small fragments of cutinite and suberinite are rare. The total amount of these macerals increases up to 7.5 vol% in the lower part of the Cypris Fm. Liptinite group macerals of aquatic origin are abundant and form, in decreasing amounts: (1) bituminite, liptodetrinite and mineral groundmass, (2) a mixture of lamalginite and lamellar bituminite positions and (3) separate telalginite bodies.

Small particles of bituminite and liptodetrinite that are poorly defined, together with clay minerals, form a mineral-bituminous groundmass (Fig. S5c). The groundmass that forms from 11.5 to 34.5 vol% claystones (Table 1) is non-fluorescent or weakly fluorescent, and only dispersed small fragments of alginite, bituminite and liptodetrinite display yellow or orange fluorescence.

A mixture of lamalginite and lamellar bituminite, classified according to Fishman et al. (2012), forms elongate positions (Fig. S5d, e). The contents of lamalginite and lamellar bituminite (1.8–43.6 vol%) rapidly increase from the base to the roof of the Cypris Fm. The lamellar bituminite, with wavy or crinkly appearance in some places, forms elongate bodies more than 30 µm thick, arranged parallel or subparallel to the bedding. Lamellar bituminite displays relatively lower fluorescence than lamellar alginite and lamalginite. Lamalginite forms discrete, thin, elongated lamellar bodies with relatively well-defined boundaries and is commonly associated with lamellar bituminite.

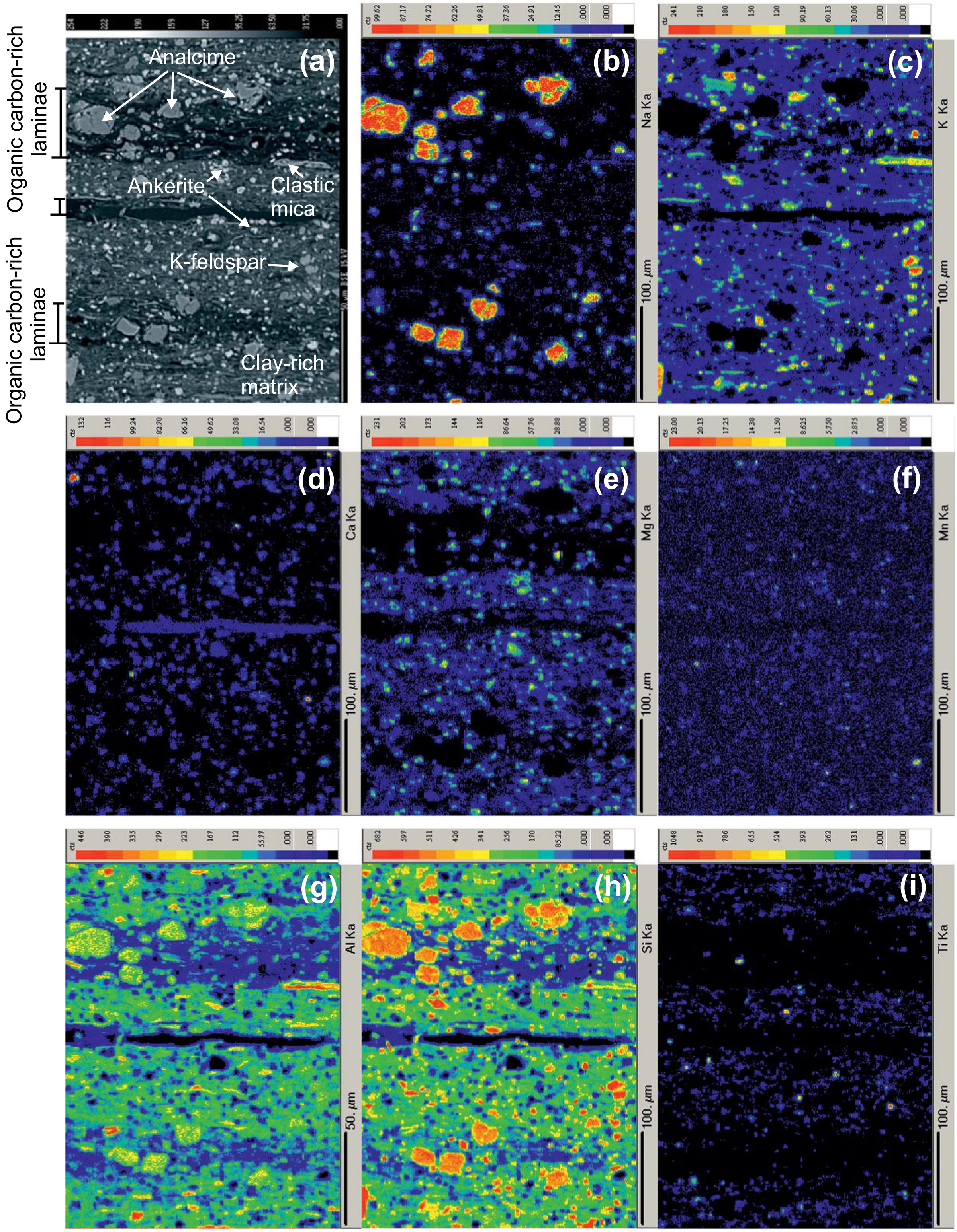
The amount of telalginite is <5 vol%. Bright yellow fluorescence was observed in telaginite (Fig. S5a, f). Its volume increases irregularly from 0.4 vol% in the lower part to 4.5 vol% in the upper part of the Cypris Fm.

Minerals in Table 1 represent the total amount of mineral matter without visible organic particles and include clay minerals, quartz grains, euhedral and framboidal pyrite, carbonates and other minerals.

Geochemistry of the Cypris Formation

Relations among variables

To understand the geochemical evolution of the Cypris Fm., relations among the variables were studied using a nonparametric correlation, principal component analysis and cluster analysis. This made it


Organic carbon-rich laminae
Organic carbon-rich laminae
Analcime
Ankerite
Clastic mica
K-feldspar
Clay-rich matrix
(a)
(b)
Na Ka
(c)
K Ka
(d)
Ca Ka
(e)
Mg Ka
(f)
Mn Ka
(g)
Al Ka
(h)
Si Ka
(i)
Ti Ka
100. μm
50. μm
cts

◀**Fig. 3** **a** A photomicrograph of the Cypris Fm. Claystone, formed by alternating layers rich in organic carbon (*dark gray*), and layers rich in clay matrix with numerous grains of analcime (Na-zeolite), clastic micas and authigenic carbonate (siderite–dolomite). The *upper part* of the Cypris Fm. (back-scattered electron distribution of individual elements); **b** areal distribution of sodium corresponds to the occurrence of Na-zeolite—analcime; **c** areal distribution of potassium corresponds to the distribution of detrital muscovite/illite, and K-feldspar; **d** areal distribution of calcium; **e** distribution of magnesium; **f** distribution of manganese. Distribution of Ca, Mg and Mn correspond to the occurrence of carbonates; **g** distribution of aluminum; **h** distribution of silicon corresponds to the occurrence of quartz; **i** distribution of titanium. Titanium is bound in either detrital anatase grains (*bright spots*) or is dispersed in a silicate matrix

possible to categorize the individual variables and to assign them to individual mineral phases. The results were used to determine the sources of the detrital material brought into the lake basin and to explain the variations in the concentrations of the individual elements during the evolution of the Cypris paleolake.

Results of nonparametric correlation of elements determined by the X-ray fluorescence method (Table S1) showed a statistically significant positive correlation at the >0.001 (99.9%) probability level among the following elements:

1. Ti, Zr, Ba, Fe, Cu and Pb
2. K, Rb and Zn
3. Ca, Sr and Mn
4. S and As

Close correlation between contents of Ti, Zr, Ba, Fe, Cu and Pb can be explained by bonds of these elements in the psammitic and psephitic components of the rocks, which are formed by the altered rock fragments from the source areas of the sediments, by grains of rutile, zircon, feldspars and ferromagnesian minerals.

Statistically significant correlation between K and Rb can be explained by the presence of high concentrations of illite in the pelitic fraction of claystones. Part of the zinc also seems to be bound in this fraction by sorption.

The correlation between Ca, Sr, and Mn indicates the presence of carbonates, especially siderite and dolomite, and the statistically significant correlation between sulfur and arsenic content reflects the presence of authigenic sulfides.

Cluster and principal component analysis was carried out on two sets of samples. The first set included all the rock samples taken from drill cores and analyzed by the PXRF method (1635 samples). The second set (90 samples) included only selected samples of claystones, in which the presence of sodium and silicon was also established by chemical methods.

Results of cluster analysis of the first group of samples are in agreement with results of correlation among the individual elements (compare Table S1, and Fig. 4a, b). The results of principal component analysis showed that the distribution of elements in the studied rocks is determined by two dominant factors:

- Factor 1, which explains 34.8% of the variability of the studied data, can be interpreted as the ratio of fine-grain (pelitic) and coarser-grain (psaphitic and psammitic) fractions of the sediment.
- Factor 2, which explains 18.52% of the variability of the studied data, can be interpreted as the amount of carbonate admixture in the sediments.

It should be noted that the plot for Fe lies between the elements characteristic of the clastic and carbonate components of the studied rocks. This indicates that this element is bound to pyrite disseminated in claystones, as well as to siderite or ankerite.

Results of cluster and principal component analyses of the second group of samples (only claystones; Fig. 4c, d) are not much different from those of the first group. Because of the exclusion of rocks with high carbonate contents, however, the relationships among Ca, Sr and Mn are not as strong because they are determined less by the content of carbonates and more by the grain-size composition of the claystones. The factor loading of Si is similar to that of Ti, Zr, and Ba, which indicates that Si is present predominantly in the form of detrital quartz. The occurrence of authigenic silica, however, cannot to be ruled out. The factor loading of sodium is similar to that for potassium and rubidium, suggesting that it is bound to the clay fraction.

Sources of sediments

To assess the sources of detrital material in the rocks forming the Cypris Fm., their chemical composition was compared with that of two possible sources: (1)

Table 1 Total organic carbon (TOC) content, Rock–Eval hydrogen index (HI; in mg HC/g TOC), huminite random reflectance (R_r; in %), and huminite, inertinite, liptinite maceral groups and mineral matrix contents (vol%) in borehole Dp 333-09

Sample depth (m)	TOC (wt%)	HI	R_r (%)	Huminite (vol%)	Inertinite (vol%)	Liptinite (vol%)					Minerals (vol%)
						Total liptinite group	Macerals of terrestrial origin	Telalginite	Lamalginite and bituminite	Bituminite, liptodetrinite and clay matrix	
4.16	7.15	754	0.15	1.2	0.4	63.9	0.5	4.5	30.7	28.2	34.5
5.76	4.39	708	0.18	1.1	0.3	54.7	0.3	2.4	24.7	27.3	43.9
6.40	–	–	0.16	1.0	2.0	50.2	0.6	3.9	21.8	23.9	46.8
8.86	4.37	711	0	0	1.4	51.1	1.0	1.3	23.6	25.2	47.5
12.06	4.34	754	0	0	0.9	48.3	0	1.2	23.3	23.8	50.8
14.96	1.32	151	0.19	0.5	2.1	20.8	0	0	4.7	16.1	76.6
16.66	4.02	690	0	0	0.8	50.6	1.5	0.8	23.9	24.4	48.6
17.26	4.29	737	0.20	0.8	0.4	49.5	1.1	1.6	26.6	20.2	49.3
19.76	4.54	735	0.20	0.5	0.6	52.7	1.8	3.3	20.8	26.8	46.2
20.26	6.41	804	0.20	0.6	1.0	53.5	0	0.7	30.4	22.4	44.9
22.36	4.58	790	0.20	0.4	0	57.5	0	0.5	26.5	30.9	42.1
25.26	5.05	737	0.20	0.5	0.5	57.6	0.4	2.6	25.4	29.2	41.4
28.36	7.02	813	0.21	0.7	0.4	63.7	0.2	2.3	33.7	27.5	35.2
31.56	8.57	868	0.20	0.9	0.3	77.4	1.1	2.9	38.9	34.5	21.4
35.46	11.2	900	0.20	0.7	0.7	79.6	0.7	1.1	43.6	34.2	19.0
35.98	–	–	0.20	1.3	0.6	32.2	1.9	2.0	11.6	16.7	65.9
38.06	1.28	302	0.21	1.8	3.3	20.3	0	0.9	5.2	14.2	74.6
45.96	2.53	626	0.22	0.8	0.4	34.7	0	1.5	12.7	20.5	64.1
46.05	–	–	0.23	0.9	0.8	38.8	4.8	1.8	10.4	21.8	59.5
47.86	5.39	811	0.22	1.0	1.4	56.9	0	2.2	26.4	28.3	40.7
48.46	–	–	0.22	1.1	0.5	34.4	0	1.9	9.5	23.0	64.0
50.16	0.52	179	0.24	1.5	0	20.1	5.7	0.7	2.3	11.5	78.4
53.17	–	–	0.26	0.3	1.4	35.6	2.7	1.1	8.6	23.2	62.7
57.10	–	–	0.28	9.4	3.0	30.4	1.9	3.2	8.9	16.6	57.2
57.18	16.81	268	0.29	26.8	2.2	27.3	11.7	0.9	1.8	12.9	43.7
57.22	–	–	0.30	15.7	4.8	34.2	14.0	2.3	4.5	13.4	45.3
57.28	–	–	0.23	0.4	0.8	36.1	1.2	1.5	10.3	23.1	62.7
62.16	0.71	294	0.22	1.3	1.0	25.2	5.2	1.1	2.6	16.3	72.5
65.76	2.25	240	0.24	1.4	1.1	33.2	7.5	0	4.6	21.1	64.3

Table 1 continued

Sample depth (m)	TOC (wt%)	HI	R_r (%)	Huminite (vol%)	Inertinite (vol%)	Liptinite (vol%)					Minerals (vol%)
						Total liptinite group	Macerals of terrestrial origin	Telalginite	Lamalginite and bituminite	Bituminite, liptodetrinite and clay matrix	
69.66	1.43	475	0.24	0.4	0.4	26.2	4.8	1.5	4.4	15.5	73.0
70.53	–	–	0.23	0.8	0.3	31.1	6.0	0.9	4.3	19.9	67.8
71.66	1.37	461	0.25	0.5	0.5	23.2	3.6	1.1	4.9	18.3	71.1
73.56	0.69	304	0.26	0.7	0.2	23.2	4.4	0.6	4.5	13.7	75.9
74.36	1.53	278	0.26	0.3	0.9	27.4	5.7	0.4	4.0	17.3	71.4

the weathered crystalline rocks and granites, and the products of their weathering (China clay) and (2) the tuffs and products of their alteration (bentonite) in the source areas. The lower and upper parts of the Cypris Fm. were thus distinguished.

Figure 5a shows the relationship between the contents of Ti and Zr. The diagram indicates that the contents of both elements in the rocks in the lower and upper parts of the Cypris Fm. correlate strongly, i.e. with increasing content of titanium, the concentration of zirconium also increases. Moreover, it is evident that the Ti/Zr ratio in the rocks follows a trend that is typical of volcanic rocks and bentonites, rather than a trend characteristic of the products of weathering of crystalline rocks and granitoids. On the other hand, the potassium content and thus the K/Ti ratio in the rocks of the Cypris Fm. are significantly higher than in tuffs and bentonites (Fig. 5b). This means that the products of weathering of crystalline rocks and granites, rich in potassium, were also major sources of the detrital component in the sediments, in addition to the volcanic material. The rubidium/barium ratio also suggests mixing of the two sources (Fig. 5c).

Geochemical evolution of the Cypris Formation

The distribution of chemical elements and their relationships were studied in two borehole lithological sections. The first was situated at the edge of the basin (borehole Dp 333-09), whereas the other was located in the central part of the basin (borehole Jp 585-09; Fig. 1). The K/Ti and K/Zr ratios in the sediments of both boreholes display similar trends, allowing correlation of the individual horizons (Fig. 6). Differences in depths of specific horizons between the two boreholes is caused by earlier onset of sedimentation in the deeper part of the basin or by differential compaction of organic matter in the process of coalification. This is also apparent in the different depths of individual marker horizons (coaly siltstone marker bed, greigite-rich horizon, carbonate-rich positions), which are used in the SB for macroscopic correlation of borehole lithology. The figure also reveals that the K/Ti and K/Zr ratios in the lower part of the Cypris Fm. are relatively constant, whereas in the upper parts of both boreholes they vary considerably.

Correlation of the two boreholes on the basis of the Ca/K and Ca/Ti ratios (i.e. the relationship between the clastic and carbonate fractions of the sediment) is

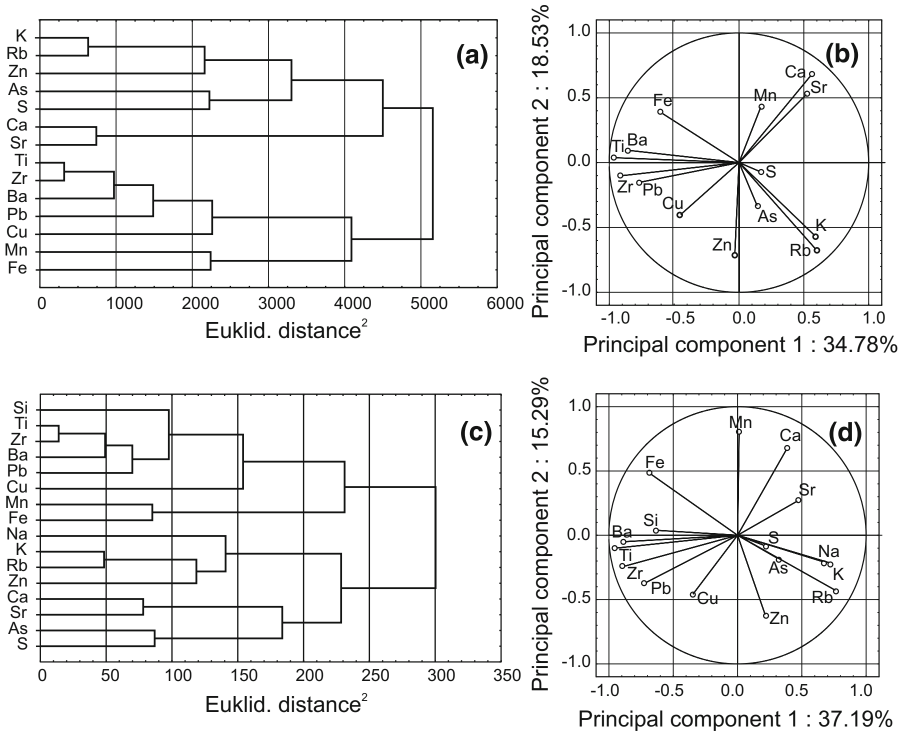


Fig. 4 **a**, **b** Cluster and principal component analysis of chemical elements in rocks of the Cypris Fm. All analyzed samples including tuffaceous rocks and carbonates (PXRF data); **c**, **d** claystones of the same formation (PXRF and chemical data) without carbonates

not as simple (Fig. 7), suggesting that part of the carbonate layers resulted from redistribution of carbonates during diagenesis. The amount of carbonate in the upper part of the Cypris Fm. is much greater than in the lower part.

The Rb and K contents in claystones show very good correlation (Fig. 4), and therefore even the Rb/Zr correlation (Fig. S6) follows the same trend as the K/Zr correlation (Fig. S6). Values of the Mn/Fe ratio in the upper part of borehole Dp 333-09 are much lower than in the upper part of borehole Jp 585-09 (Fig. S6).

Because the sulfur in both boreholes is bound in both sulfides and gypsum, the concentrations of arsenic were used as a proxy for the distribution of sulfides. There were horizons, however, that would enable correlation between the two boreholes (Fig. S6). This demonstrates that sulfide distribution is controlled mainly by diagenetic processes. The amount of arsenic (and thus sulfides) is approximately equal in both boreholes. Ratios of sodium and other elements in the claystones of both boreholes (Fig. 8) argue for a rapid increase in sodium content in the upper part of the Cypris Fm.

Overall concentration of silicon increases from the bedrock to the roof of the Cypris Fm. (not shown). Similarly, Si/Ti and Si/Zr ratios increase (Fig. 9a, b). Although the Si/K and Si/Ca ratios increase from the bedrock to the roof, there is an exception in the uppermost part of borehole Jp 585-09. The decrease in the Si/K and Si/Ca ratio is probably a consequence of greater increases in the clay and carbonate fractions relative to silica (Fig. 9a, b).

Discussion

Geochemical trends in the development of the Cypris Formation

The most significant long-term trend in the lake sediment is the decrease in the K/Ti and K/Zr ratios from the bedrock to the roof of the section (Fig. 6), which can be explained in two ways: (1) gradual diminution of tectonic activity, i.e. decreasing rate of subsidence of the basin floor, thus reducing the height differences between the source areas of the clastic

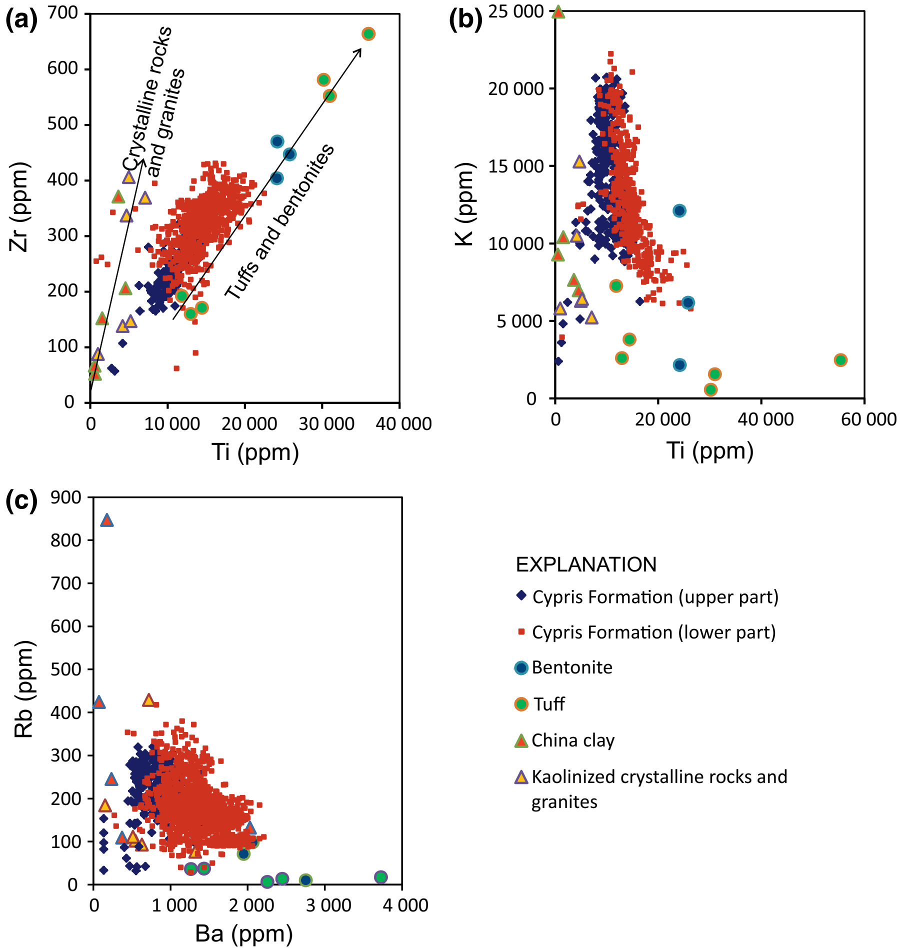
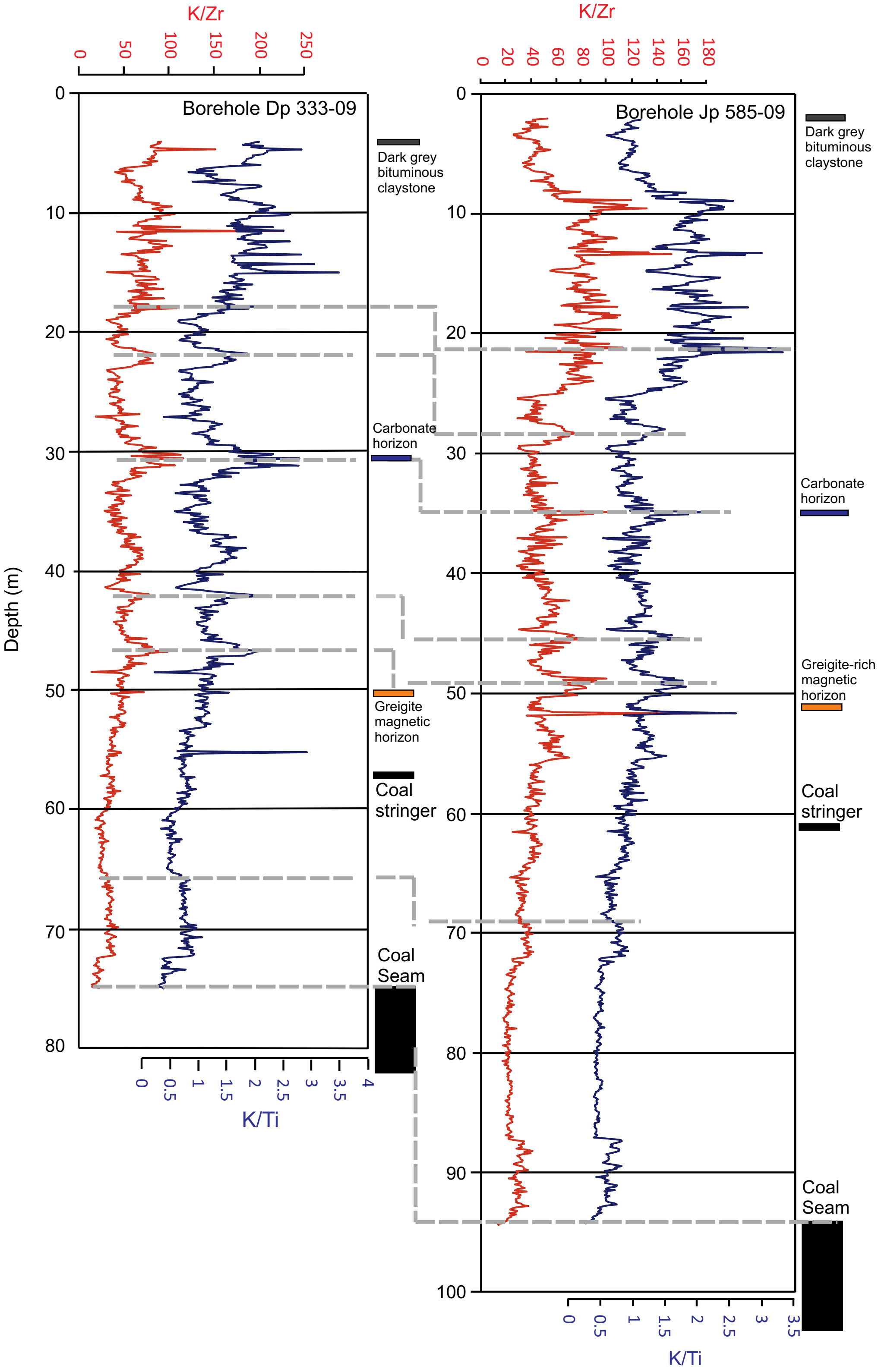


Fig. 5 The contents of Ti, Zr, and Ba in rocks of the Cypris Fm. compared with their concentrations in the products of weathering of crystalline rocks, granites, tuffs and bentonites in source areas. Proportions of the individual elements prove that the detrital component of the sediment was derived from both volcanic activity and weathering of gneisses and granites

components of the sediments and the lake, or (2) changing proportions of the clastic constituent from various sources, i.e. the products of older or synchronous volcanism, and products of long-term weathering of crystalline rocks and granites.

The relationship between stream velocity and grain-size composition of the suspended material is generally known (Potter et al. 1980). The amount of transported, coarse-grained material decreases with a decline in stream velocity. Results of cluster and principal component analysis showed that, although Ti, Zr, and other elements (Ba, Pb and part of the Fe) are confined to the psammitic and psephitic fraction of the sediments, potassium and rubidium are bound in the pelitic fraction. The increasing trend in potassium and rubidium content and, conversely, the decline in the concentrations of Ti and Zr, and other elements confined to the psammitic or psephitic fractions of sediments of the Cypris Fm. from its base to the top, may therefore indicate a reduction in the energy of streams that transported clastic material into the lake basin.

The gradual increase in the amount of K, and the decrease in the concentrations of Ti from the Oligocene to the Middle Miocene in basins of the Ohře Rift system were discussed by Elznic et al. (1998), who was of the opinion that this trend was a consequence of successive depletion of the volcanic (tuffitic) component in the deposited sediments and, conversely, an increase in the clastic constituent, derived from the weathered surface of the exposed crystalline rocks and granitoids. The Ohře Rift is a half-graben that is sharply bordered on the NW side against the crystalline unit of the Krušné Hory (Erzgebirge) Mountains by a series of downslip faults, whereas tectonic constraints are far less obvious on the


K/Zr
0
50
100
150
200
250
Borehole Dp 333-09
Depth (m)
0
10
20
30
40
50
60
70
80
Dark grey bituminous claystone
Carbonate horizon
Greigite magnetic horizon
Coal stringer
Coal Seam
0
0.5
1
1.5
2
2.5
3
3.5
4
K/Ti
K/Zr
0
20
40
60
80
100
120
140
160
180
Borehole Jp 585-09
0
10
20
30
40
50
60
70
80
90
100
Dark grey bituminous claystone
Carbonate horizon
Greigite-rich magnetic horizon
Coal stringer
Coal Seam
0
0.5
1
1.5
2
2.5
3
3.5
K/Ti

◀**Fig. 6** Boreholes Dp 333-09 (marginal part of the basin) and Jp 585-09 (central part of the basin) and correlation of the K/Zr and K/Ti ratios. Both ratios indicate the relationship between the pelitic and psammitic fraction of the sediments. Correlations between the two boreholes are indicated by *gray dashed lines*. The diagram also shows some markers that are used in macroscopic correlation of drill cores and their lithology in the field (head of the coal seam, coal stringer, greigite-rich horizon, carbonate horizon and *dark-gray* bituminous claystone)

SE side. It is therefore understandable that subsidence of the basin floor in the adjacent area of downslip faults was very high, and was responsible for the gradual prevalence of the products of weathering of crystalline rocks rich in kaolinite and illite, over volcanic material. This possibility is also supported by indications of delta sedimentation (Čankov sands; Fig. 2), which mainly occur along the NW edge of the Sokolov Basin, i.e. in the area adjacent to the Krušné Hory Mts.

The Rb/K ratio, similar to the K/Ti and K/Zr ratios, also increases upwards in the Cypris claystones, in particular in borehole Jp 585-09 (Fig. S6). The increase in the Rb/K ratio in the lake sediments is considered by some to be proof of elemental fractionation during weathering (Roy et al. 2008a). Whereas potassium in the weathering crust is bound to emerging illite, the rubidium is released into solution (McQueen 2008). The gradual increase in the Rb/K ratio in Cypris sediments may therefore be explained by an increase in the rubidium concentration in the waters of a closed lake during its evaporation and by sorption of Rb onto clay minerals.

The Mn/Fe ratio is used as a proxy for syn- and post-depositional redox conditions in the bottom waters and sediments of lacustrine systems (Naeher et al. 2013) because Fe and Mn have different Eh stability fields, with Mn exhibiting higher solubility under less oxic conditions (Davison 1993). The authigenic, redox-driven Mn/Fe pattern can, however, be overridden by the allogenic input of Mn and Fe.

A gradual rise in temperature in the Lower Miocene and thus increased evaporation were inferred by Mach et al. (2014), based on paleoclimatic analyses in the neighboring Most Basin (Fig. 1) which, like the Sokolov Basin, belongs to the Ohře Rift system. Evidence of thermophilous and later, paleosubtropical elements in latest Lower Miocene sediments of the Most Basin was considered by Teodoridis and Kvaček (2006) and Mach et al. (2014) to reflect the onset of the Miocene Climatic Optimum, a phenomenon of global importance (Mosbrugger et al. 2005; Zachos et al. 2001).

A gradual transition from humid to more arid conditions, closing of the lake, and an increase in the water salinity/alkalinity from the base to the top of the Cypris Fm. are clearly indicated by the gradual increase in the Na/Zr and Na/Ti ratios (Fig. 8). Sodium in the Cypris Fm. claystones is present especially in zeolite-type minerals, e.g. analcime (Figs. 3, S4). This mineral is reported from both fossil and modern saline lacustrine environments (Surdam and Eugster 1976; English 2001; Roy et al. 2006). In pyroclastic sediments, it is formed by a diagenetic reaction between saline solutions and precursor volcanic glass (e.g. Lake Magadi, Kenya). Analcime, however, is also reported for saline lake formations without any volcanic admixture, e.g. Lake Natron, Tanzania; Lake Lewis, Australia; Sambhar and Didwana Playas of the Thar Desert, India and San Felipe Paleolake in the Sonora Desert, Mexico (Roy et al. 2010). In saline, silica-deficient environments, the preexisting volcanic glass or aluminosilicates become unstable and partially break down to form an amorphous aluminosilicate gel enriched in relatively insoluble Al and Si. Soluble cations such as Mg, Ca, and Na are expelled from the crystal structure of silicates. Later, by incorporating Na and H_2O from brine, the amorphous gel diagenetically evolves to analcime (Drever 1982; English 2001). In addition to analcime, part of the sodium may also be bound in the pelitic fraction of the sediment, i.e. in the smectite group of minerals, as indicated by the results of the cluster and principal component analyses of claystones (Fig. 4c, d).

The gradual increase in the Si/Ti and Si/Zr ratios (Fig. 8) also appears to be a long-term trend in the development of the Cypris Fm. Because of very limited evidence of the formation of biogenic silica, this trend is considered to be an indication of desiccation of the basin, and incursion of eolian quartz. This also corresponds to the amount of fine particles of quartz and mica on bedding planes of claystones in the upper part of the Cypris Fm. (Rojík et al. 2014). We cannot, however, exclude the possibility that, as a consequence of evaporation, supersaturation of the basin water with silicon and

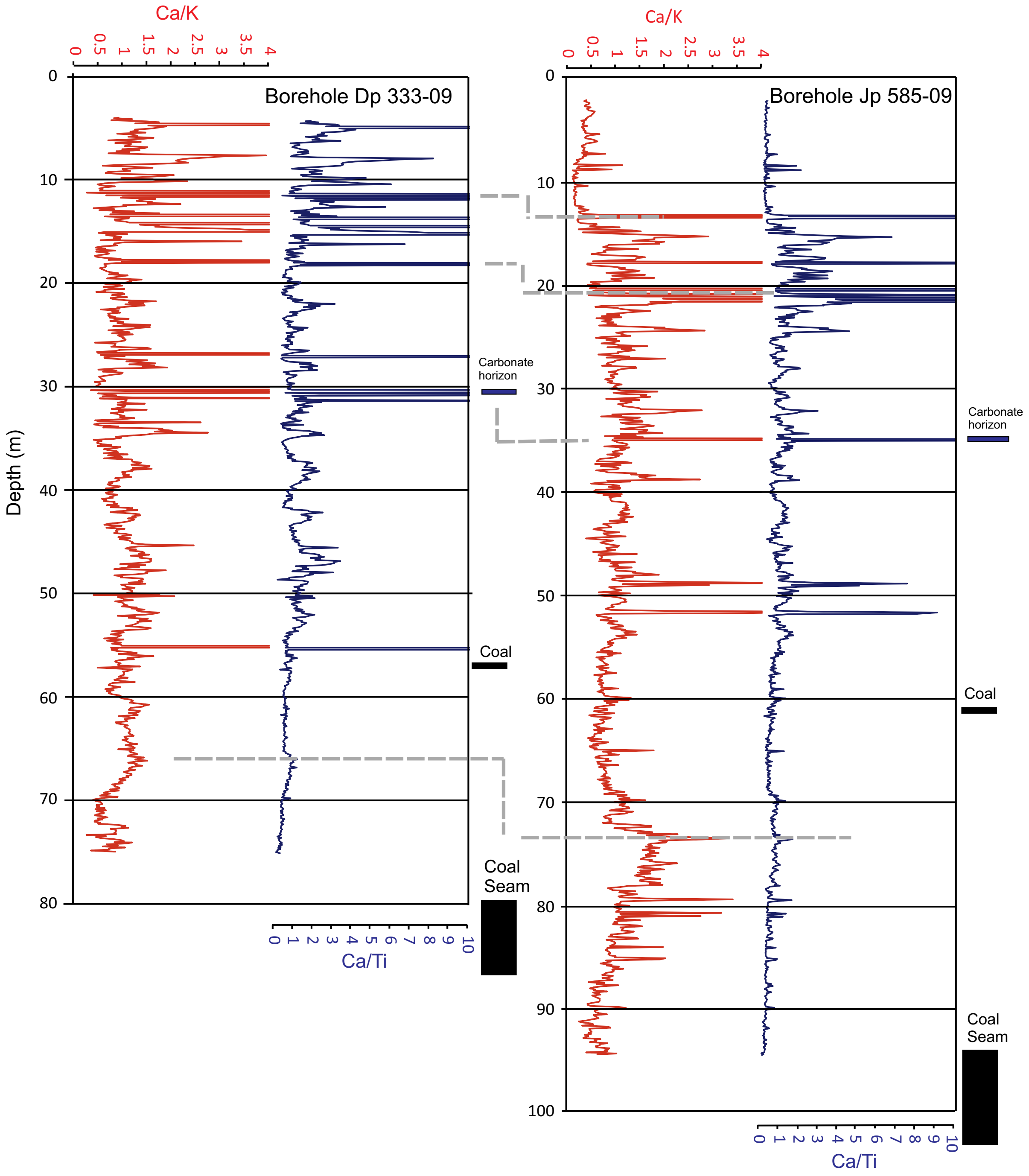


Fig. 7 Boreholes Dp 333-09 and Jp 585-09 and correlation of the Ca/K and Ca/Zr ratios. The high values of both ratios indicate the presence of carbonate beds. For an explanation, see Fig. 6

subsequent inorganic precipitation of amorphous SiO_2 might have occurred.

Gradual closing and desiccation of the lake during sedimentation of the Cypris Fm. is supported by results of isotopic studies of synsedimentary or early diagenetic carbonates (dolomite and siderite), which form numerous stratiform positions in the upper part of the Cypris Fm. The $\delta^{18}O$ values of the carbonates

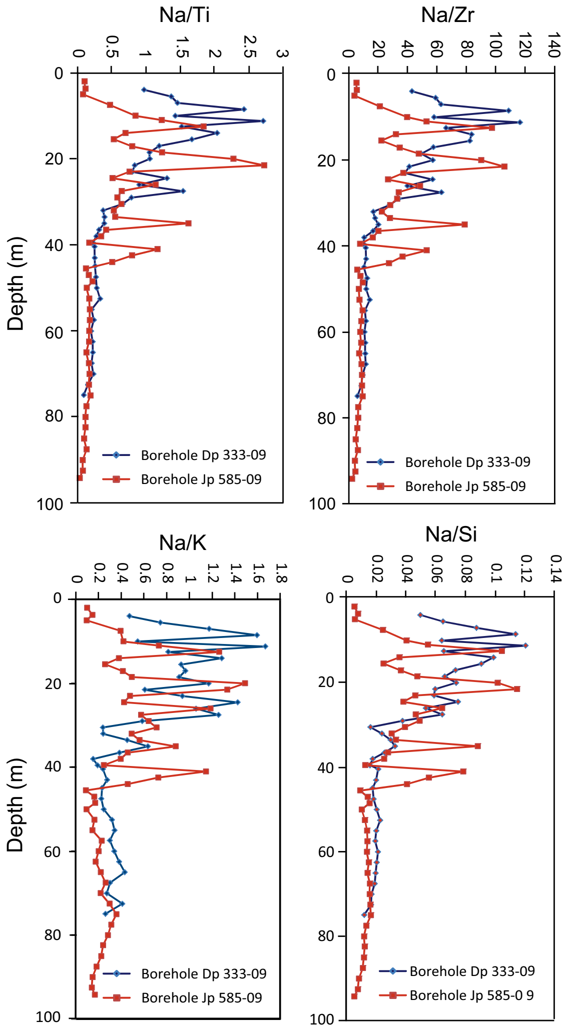


Fig. 8 Boreholes Dp 333-09 and Jp 585-09 and the Na/Ti, Na/Zr, Na/K and Na/Si ratios in both boreholes

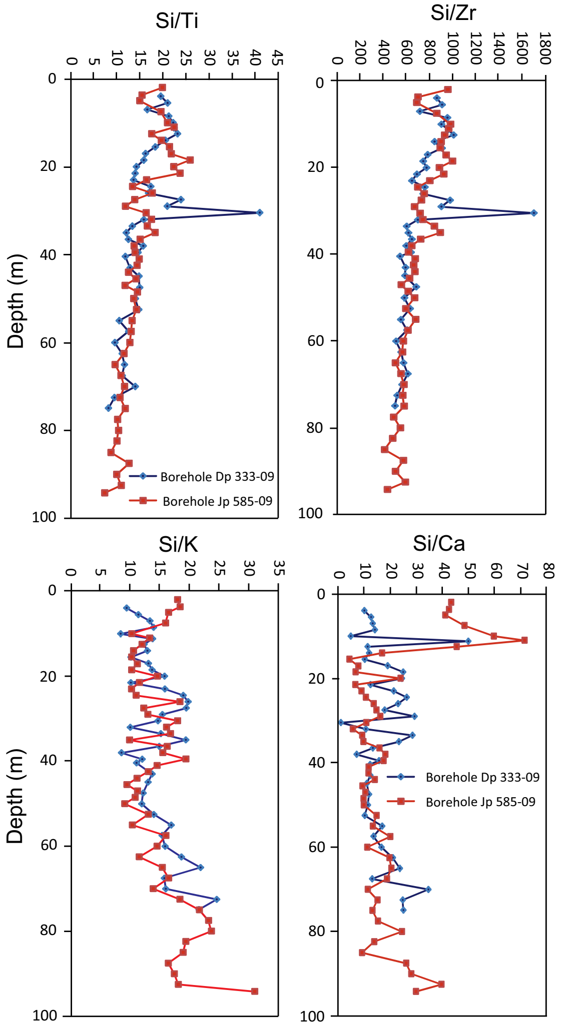


Fig. 9 Boreholes Dp 333-09 and Jp 585-09, and the Si/Ti, Si/Zr, Si/K, and Si/Ca ratios in both boreholes

range between +30.2 and +37.5‰ (V-SMOW; Šmejkal 1976). At the average temperature during the Lower Miocene in Europe, which was believed to have been between 15 and 20 °C (Zachos et al. 2001; Böhme 2003), these values correspond to δ^{18}O of water in the sedimentary basin in the range +3.0 to +4.0 (V-SMOW). This means that the oxygen isotope value of water in the Miocene lake was about 3.0–3.5‰ enriched relative to the oxygen isotope value of contemporary seawater. According to Šmejkal (1976), this argues for a long process of evaporation in a closed basin, which resulted from increasing temperature. The calculated values of the isotopic composition of the water during the precipitation of carbonates, which are confined especially to the upper part of the studied profile, correspond to the values that Renac et al. (2013b) reported for water in Miocene closed basins in the Massif Central (δ^{18}O = +2.9 to +4.2‰).

The δ^{13}C values of synsedimentary dolomites in the Cypris Fm. range between +2.5 and +14.8 (mode: +9.8‰ V-PDB) and are correlated significantly with the δ^{18}O values (Šmejkal 1976, 1984). This correlation indicates that the δ^{18}O and δ^{13}C values are controlled by the same process. Oana and Deevey (1960) found that, in undrained alkaline continental lakes, both δ^{13}C and δ^{18}O values in synsedimentary or early diagenetic carbonates increase with increased evaporation. This phenomenon is often referred to as covariance of $\delta^{13}C$ and $\delta^{18}O$ values (Li and Ku 1997). For example, high values of $\delta^{13}C$ and $\delta^{18}O$ were detected in the extremely saline environment of Searles Lake, where the $\delta^{13}C$ values of carbonates varied between 0 and +10‰, V-PDB (Stuiver 1964). On the basis of isotopic studies of O and C in carbonates of the Middle Miocene rift basins of the Massif Central in France, Renac et al. (2013a) also believed that high $\delta^{13}C$ and $\delta^{18}O$ values of carbonate beds were a consequence of an increase in temperature, increasing the evaporation/inflow ratio, and gradual desiccation of the lake. The matter, however, is much more complex. In addition to climate and hydrological changes, the relation between $\delta^{13}C$ and $\delta^{18}O$ in hydrologically closed lake basins is also influenced by biological productivity in the lake, pH of the lake water and other factors (Li and Ku 1997).

The concept of gradual closing of the Cypris Lake is also supported by enrichment of sulfides (pyrite) with the ^{34}S isotope ($\delta^{34}S$ = +7.2 to +45.1 ‰, V-CDT; Šmejkal 1978). The enrichment of sulfides in ^{34}S was explained as resulting from the escape of light bacterial H_2S during the initial (open) stage of basin development, and by the origin of the heavier isotope in hydrogen sulfide from the residual, isotopically heavier sulfate in the environment of a hydrologically closed basin, under conditions when evaporation exceeds replenishment of sulfates by freshwater streams.

The relatively high salinity/alkalinity of the water, at least during some intervals of the upper part of the Cypris Fm. is demonstrated by the occurrence of halophilous aquatic vegetation including remnants of *Limnocarabus*, whose recent, related genus *Ruppia* grows only in high-mineral waters; Bůžek and Holý 1981; Kvaček et al. 1987). Formation of carbonate duricrusts with desiccation fissures and convolute structures on their bottom surface, also suggests that the lake experienced multiple phases of episodic drying (Rojík et al. 2014).

The content of liptinite-group macerals of aquatic origin generally increases from the base to the roof of the Cypris Fm. (Fig. 10). This maceral group is composed mostly of a mixture of bituminite, liptodetrinite and clay minerals, and of lamalginite and bituminite. Bituminite is generally referred to as a product of bacterial degradation of primary biomass, such as algae, bacterial lipids, degraded animal plankton and other precursors (Rimmer et al. 2004; Havelcová et al. 2012). Bacterial reworking of the original organic matter is documented by a large amount of bacterial or cyanobacterial terpenoids (hopanes) (Kříbek et al. 1998). The lamalginite is derived from small, unicellular or thin-walled, colonial plankton or benthic algae that live in the photic zone of shallow lakes and seas (Teichmüller and Ottenjan 1977; Taylor et al. 1998). The content of telalginite, which is derived from colonial or thick-walled unicellular algae such as *Botryococcus* or *Tasmanites* (Teichmüller and Ottenjan 1977), is low compared with bituminite, liptodetrinite and lamalginite, and increases only slightly from the lower part to the upper part of the Cypris Fm.

The content of liptinite-group macerals of aquatic origin correlates well with values of the hydrogen index ($HI_{Rock\ Eval}$; Fig. 10) and content of TOC (Table 1), and increased along with an increase in the sodium content from the bedrock to the roof of the Cypris Fm. (Fig. 10), thus arguing for a gradual increase in the activity of algae and for

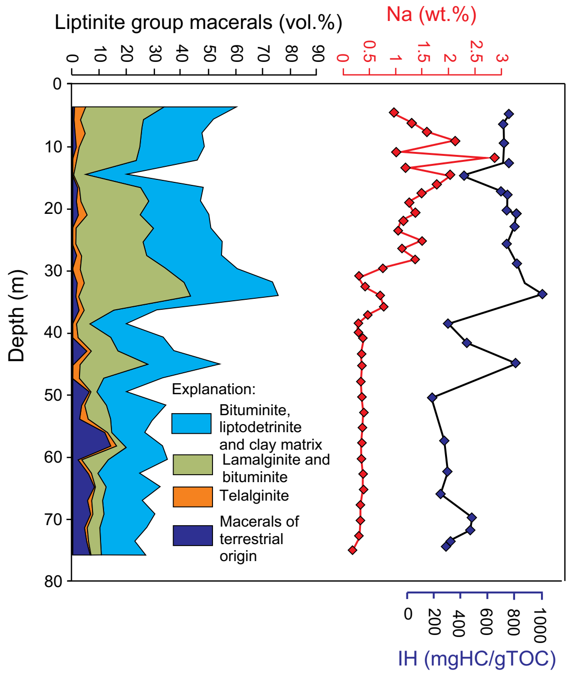


Fig. 10 The content of liptinite-group macerals, sodium concentrations and hydrogen index values ($HI_{Rock\ Eval}$) in the claystones of borehole Dp 333-09. Classification of the liptinite-group macerals after Fishman et al. (2012)

eutrophication of the lake environment with increasing salinity/alkalinity. Eutrophication of the pristine saline/alkaline environment usually occurs as a consequence of an increasing amount of dissolved phosphorus, which is rapidly released in an alkaline medium during rock weathering, particularly those containing volcaniclastic material. The P_2O_5 content in volcanic rocks, particularly in their alkaline equivalents, in the area of the Ohře Rift, ranges between 0.26 and 0.93 wt% (Cajz et al. 2009) and reaches 1.1 wt% in alkaline intrusive rocks (Skála et al. 2014). Phosphorus may also be recycled during mineralization of the organic matter of the sediment (Schettler et al. 2006).

In contrast to the increasing content of liptinite-group macerals of aquatic origin and $HI_{Rock\ Eval}$ values toward the top of the Cypris Fm., the content of liptinite-group macerals of terrestrial origin (liptodetrinite, bituminite, alginite, sporinite and resinite) gradually decrease (Fig. 10), which can be related to a decrease in the productivity of the terrestrial biota. Aeolian transport is assumed to be responsible for most of the terrestrial organic input (Sabel et al. 2005; Havelcová et al. 2015).

Repetitive changes in the geochemical composition of the Cypris Formation

Besides the long-term trends in geochemical evolution in the Cypris Fm., repetitive changes are also observed in their chemical composition on different time scales. On a microscale, there are laminae with layers rich and poor in organic matter, on a scale of 10–50 µm (Figs. 6, S3). These laminated sediments, without any sign of bioturbation, were probably deposited under anoxic conditions at the bottom of the lake. Laminae rich and poor in organic matter have relatively low carbonate content, and their alternation may be explained by

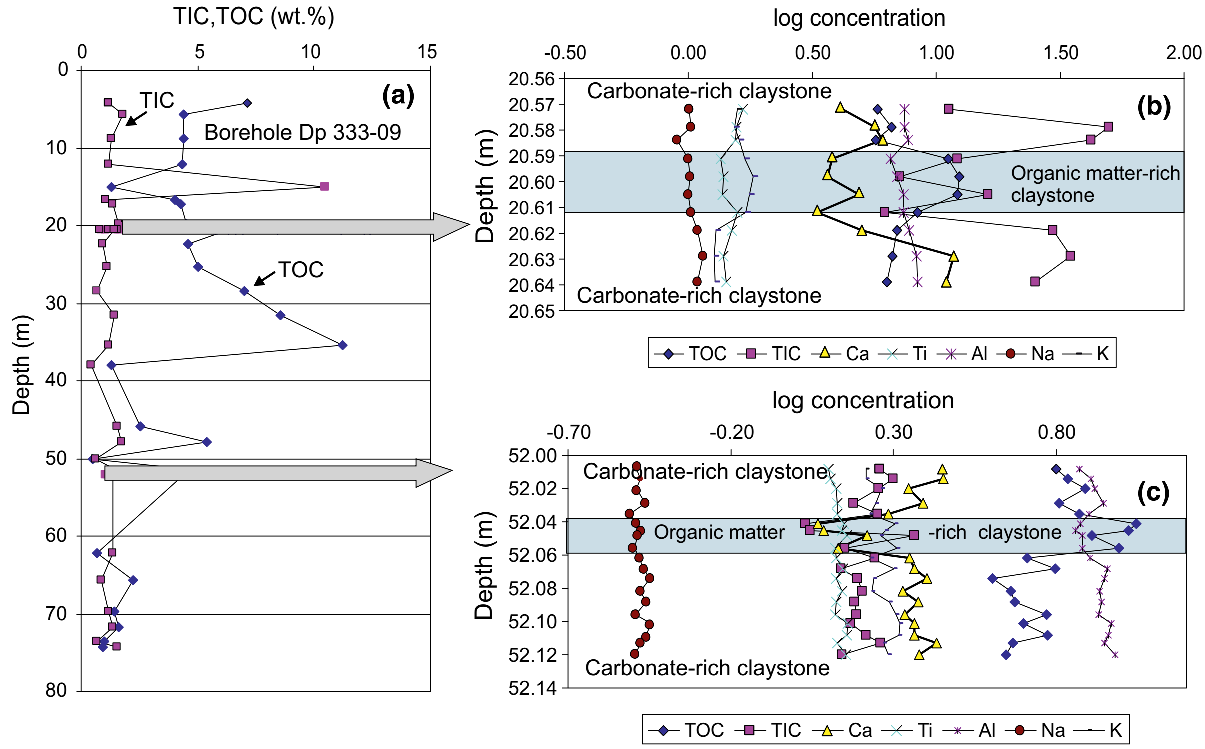


Fig. 11 **a** The contents of total organic carbon (TOC) and total inorganic carbon (TIC) in borehole Dp 333-09; **b**, **c** alternation of layers rich in organic carbon with carbonate positions in two microsections sampled in the lower and upper parts of the Cypris Fm. in the same borehole. Carbonate and carbonaceous claystone layers differ only in the contents of TOC and TIC. The contents of other elements, such as Ti or Zr in carbonate-rich and organic matter-rich claystone positions, are roughly the same, which indicates a constant rate of clastic sedimentation during the deposition of both types of sediment. The concentrations of chemical elements in log ppm, concentrations of TIC and TOC in log wt%. Note the higher contents of sodium in the upper microsection of the profile, which correspond to an upward increase in the sodium contents in the Cypris Fm

different proportions of biogenic and siliciclastic material. Lamination of this type tends to reflect seasonal changes. Layers with a greater amount of organic matter originated in the period of maximum productivity of algae in the spring and summer months, whereas layers poor in organic matter probably developed during the winter months (Potter et al. 1980).

The layers of laminated claystones in the Cypris Fm., especially in its upper part, often alternate with carbonate beds, whose thickness varies from a few centimeters to decimeters (Figs. S7, 11). Because the precipitation of carbonates is controlled by temperature and pH (alkalinity) of the aquatic environment, the alternation of carbonate- and organic matter-rich sediments indicates a longer period of higher temperatures and higher evaporation, which could have led to supersaturation with $CaCO_3$, with longer periods of lower temperatures when the lake water was undersaturated. The distance from carbonate equilibrium may be affected by photosynthesis (elevated pH), and respiration (decrease in pH) (Stumm and Morgan 1970).

Repetitive changes in the geochemical composition of the Cypris Fm. claystones on a scale of meters to tens of meters are seen especially in the K/Zr and K/Ti ratios, and to a lesser extent in the Ca/K and Ca/Ti ratios, excluding carbonate beds (Figs. 6, 7). Such repetitive changes were studied by Matys Grygar et al. (2014) in the neighboring Most Basin (Fig. 1), and are explained as having resulted from orbital forcing, i.e. precession, obliquity and short eccentricity cycles. Repetitive changes that are at least partially connected with tectonic development of the area, particularly changes in the rate of subsidence of the Ohře Rift, cannot, however, be excluded. The changing rate of compaction of the underlying coal seams during coalification might have also played a role.

Conclusions

The scarcity of continental paleoclimate records during Lower Miocene times makes the Sokolov Basin a valuable region for investigation. Geochemical proxies demonstrate that the lacustrine Cypris Fm., which was the subject of this study, originated in the continental rift lake basin, which collected river water and intracontinental runoff that developed chemically during evaporation, leading to a gradual increase in the amount of sodium in the lake water and resulting in the formation of a smectite-analcime mineral assemblage. Moreover, the precipitation of calcite from the water formed ~10-cm or dm-scale beds with no recognizable laminations, suggesting a hydrologically closed lake environment during the late stage of the basin evolution. The increasing salinity/alkalinity of the aquatic environment led to temporary or permanent density-induced stratification of the lake water and gradual eutrophication of the lake. The eutrophication could have been caused by the release of phosphorus during a reaction between the volcaniclastic component and basinal brines. Sediments of the Cypris Fm. display a number of repetitive changes in their geochemical composition on a scale of micrometers to several meters. These variations were probably controlled by seasonal climate changes (microlamination of claystones) or by variations in temperature and rainfall over longer time periods (alternating layers of carbonates and organic-carbon-rich claystones). Repetitive changes in the proportion of clayey and coarser fractions in claystones can be explained by either variability of stream velocity during changes in temperature and atmospheric precipitation, or by tectonic processes, especially by the changing rate of basin floor subsidence in the Ohře Rift system. Results of this study demonstrate that the use of geochemical proxies in stratigraphic analysis enables us to gain knowledge about the paleogeography and paleoclimatology of the lake environment, and also permits the use of these data for correlation of distinct horizons within lithologically monotonous formations, which would otherwise be difficult to distinguish.

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