Slovak Geol. Mag., 6, 2-3(2000), 231–233

Geochemical methods in high resolution stratigraphy of the Early Aptian Koňhora Formation

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Abstract: The analysis of the Koňhora Formation in the Rochovica section illustrates correlation abilities of the C-stratigraphy in the Tethyan sections. The correlation was stated between positive $\delta^{13}C$ -event and global climatic perturbations, lasting 2 to 2.4 millions of years. Black shales with locally raised TOC (0,5 to 3 %) are inserted in a pale pelagic limestone sequence. Large part of organic matter has decayed and only slightly disequilibrated the $\delta^{13}C$ ratio of the C oceanic reservoir. The $\delta^{13}C$ value decreased due to overproduction of organic matter and the redox conditions moved towards the anoxia.

Key words: Isotope stratigraphy, organic geochemistry, black shales, illite/smectite, lower Aptian, Selli Event, Pieniny Klippen Belt, Western Carpathians

Introduction

Besides of their economic importance, oil-prone black shales in Jurassic-Cretaceous pelagic carbonate formations yield informations on global paleoceanic and/or paleoecological changes at that time. Lower Aptian black-shale type Koňhora Formation in the Rochovica section (Pieniny Klippen Belt) records a worldwide oceanic anoxic event (1a OAE), an equivalent of the Selli Event in the Western Carpathians (Lintnerová et al. 1997, Lintnerová 1999, Michalík et al. 1999). Precise correlation of this type formations is enabled by high-resolution $\delta^{13}C$ stratigraphic method (Menegatti et al. 1998, Weissert et al. 1998, Hochuli et al. 1999). A combination of further chemostratigraphic parameters (chemical composition, microelement distribution, TOC, kerogene type, vitrinite reflectance and mineralogical analysis of clay minerals) promoted to document sedimentary environment of the Koňhora Formation. Several questions like the relationships between $\delta^{13}C$ curve and local organic matter accumulation, or reliability of correlation between carbon isotope ratio shift and anoxia record in the sedimentary environment remain open, still.

Methods

In addition to former sample set (17 specimens), taken during last several years from Barremian-Aptian part of the Rochovica section (Michalík et. al. 1995, 1999) for high-resolution $\delta^{13}C$ stratigraphy purposes, new sample set from the Koňhora Formation has been selected. 48 samples have been taken in 25 cm sampling intervals. Geochemical and clay mineralogical composition has been ananalysed. Isotope C and O analyses were performed in laboratories of ETH Zürich and of Czech Geological Institute, Prague (Michalík et al. 1999).

X-ray-fluorescence and spectrochemical methods were used in the whole rock and microelement analysis (SAS Geological Institute).

Clay minerals were characterised by X-ray diffraction analysis using separated fine-grained fraction of samples. Semiquantitative proportions of clay minerals were estimated by simple normalization of most intensive basal reflections of individual constituents to the 100%. The content of expandable layers in mixed-layer illite/ smectite (I/S) as well as the type of interstratification were determined using techniques of Środoń (1984).

Leitz microscope (incident white and fluorescence light) with the MPV-Compact microphotometer were used to analyse the quality and quantity of sedimentary organic matter in polished sections. Microscopically determined oxidized to non-oxidized phytoclasts derived from dry-land (O/N parameter) was tested to indicate progradational-retrogradational and proximal-distal trends (Bombardiére & Gorin 2000). Total organic and inorganic carbon contents (TOC, TIC) were measured on the C-MAT 550 equipment. Rock-Eval pyrolysis was used to determine the concentrations of free and fixed hydrocarbons (S1, S2), maximum pyrolysis temperature (Tmax) and hydrogen index (HI).

Lithofacies

The Koňhora Formation represents an intercalation of shaly sediments in a pelagic majolica - type carbonate complex (see Michalík et al. 1999). Three more-or-less complete cycles are recognizable in cca 6-7 meters thick sequence of dark limy shales, marls and limestones (Fig.1.). Every one of them starts with dark brown-grey silty claystone with amount of terrestrial plant fragments and pollen grains. Limy (10-50 % $CaCO_3$), organic matter and pyrite content increase upwards. Black marly shales

in the uppermost part of cycles terminate by radiolarian limestone to radiolarite layer. The upper cycles with occasional intercalations of marly limestone are typical with increase of planktonic foraminifers, calcareous dinoflagelates and nannoplankton.

Notes to sequence stratigraphy

Twelve sequence stratigraphic systems, each cca 0.8 my in duration, are distinguishable in Aptian part of the section studied (Fig.1.). Thick biomicrite layer with fine carbonate debris and occasional chert nodules represents the typical lowstand system tract in a pelagic limestone sequence. Transgressive stand sediments are well bedded, frequently containing fluxoturbiditic intercalations. Highstand system tract record is indicated by thin bedding and more distinct marly interlayers. Brown-grey clayey shales with rich admixture of clastic quartz, mica and terrestrial phytodetrite denotes the lowstand part in the Koňhora Formation. Disseminated organic matter, fish scales and pyrite content become abundant upwards. Upper part of claystone beds passes into sapropelic black shale. The highstand is represented by radiolarian limestone (radiolarian- sponge packstone), in upper cycles of the formation by pelagic limestone containing accumulations of planktonic foraminifer and nannoplankton tests.

The sedimentation rate of pelagic limestones of both the Pieniny Limestone Fm. and Brodno Fm. was roughly equal, reaching approximately 1.2 to 1.5 mm/ka. On the other hand, the Koňhora Formation was accumulated more rapidly, with twice higher rate (2 to 2.5 mm/ka). The Koňhora terrigene event in a pelagic carbonate deposition lasted about 2.5 million of years (including the part equivalent to the Selli Event, which was laid down during about 1 million of years).

Organic matter

Carbonate content depends on stabilisation of marine conditions, environmental temperature rise and production of microplankton with calcareous tests. Organic carbon contents (TOC) reached 0.05 to 3.23 wt % values in the profile studied. Two principal types of organic matter were distinguished by microscopic investigation of claystone to limestone rocks, they differ by preservation (oxidisation) and diagenetic transformation. However, both Tmax (434 – 438 °C) and the mean vitrinite reflectance value (Rr = 0,55%) indicate only low thermal alteration of organic matter during burial.

The lowest value of the hydrogen index (HI) has been found in brown-grey shales (only 44 mg HC/g Corg). It means that a terrestrial type of organic matter is present here. This result is in agreement with an optical study: we could registrate only fusinite and oxidized vitrinite particles in polished sections. The O/N ratio is high (sample Roch 417,45) in sea level highstand part of the second cycle.

Maximal values of HI were recorded in black or dark-grey shales and in sapropelic shales (243 – 336 mg HC/g Corg. – in samples Roch 416.65, 418.4 and 418.65), containing marine and terrestrially derived organic matter. Microscopic study evidences the same results. Frequent marine algae with continental plant debris were observed in polished sections. Terrestrial material comprises of fusinite, semifusinite, sporinite, vitrinite and liptinite. O/N ratio is very low due to presence of fresh (non-oxidized) vitrinite. It probably indicates prograding transgression in the second and third cycles. Enhanced influx of nutrients to the marine environment stimulated high algal productivity and the terrestrially-derived organic material provided an additional sink of oxygen resulting in promoted anoxia (Wenger & Barker 1986). According to microscopical fluorescence study, numerous fish remnants and rests of marine algae seem to support our results.

Mineralogical and chemical characteristics of siliciclastic material

Carbonate content changes due to terrigene siliciclastic input, which decrease upwards: from 52 to 84 % in the first and second cycle to 14 až 43 % in the third one. The quantitative evaluation showed that the main part of siliciclastics consists of quartz, plagioclase, micas and clay minerals. Quartz share forms 30 to 40 % of siliciclastic material.

Within the sequence studied, no systematic variations in contents of clay minerals have been observed. The clay fractions consist of discrete illite + I/S, corrensite-like mixed-layered chlorite/smectite or chlorite/ vermiculite and chlorite with average ratio of 7:2:1. The more expressive change of smectite content in I/S was recorded in bed 409: an abrupt increase from 20-25 %S to 40-50 %S, which persists up to bed 437 (with one exception recorded in the sample 418.6 where expandability of the I/S reaches 75 %S).This is also accompanied by a decrease of degree of ordering in the I/S from R1 to R0 or R0.5. As the burial effect is not considered here, sudden change of I/S properties might be related to the change of provenance of siliciclastic material and/or change of climatic conditions during sedimentation/early diagenesis (e.g. Hartmann et al. 1999).

Geochemical characteristics

Silt quartz share, but also the presence of radiolarian silicites are indicated by raised SiO_2 content in rock analyses, or in Si/Al ratios variation, respectively. Remaining elements ratios with Al or Ti, respectively, show stability of the siliciclastic material source. The variegate calcium content is influenced by a presence of carbonates. The change of redox conditions in lime shales or early diagenetic processes in the sediment can be indicated either by changes in Ca/Mn or Ca/Fe ratio. Relatively low Mn content (25 - 139 ppm) and its correlation with the siliciclastics, indicates anoxic conditions, too (Quinsby-Hunt & Wilde 1996, Calvert & Pedersen 1996). Raised Mn content in some samples (478 - 629 ppm) from brown claystones is accompanied by reduced (relict) content of organics, indirectly indicating the presence of oxidants (sulphates, nitrates) in bottom water, or in sediment. They resulted in mentioned oxidation to decay of organics and the pyrite formation in sediment. V values of 50 to 150 ppm indicate

changing ratio of marine algal kerogene and/or relative decrease of TOC consumed by reduction in comparison with the original content. Similarly to Mn, there is no clear correlation between the V and TOC contents. The highest V (and partially also Ni) values were recorded in samples with marine kerogene. High Ba value has been recorded in several samples. As the barium can serve as a bioproduction indicator, the Ba/V correlation observed practically excludes any barium diagenetic remobilisation (Belanca et al. 1999).

Isotope record

The presence of the "Selli Event" (the first 1a OAE in the lower Aptian sequence, cf. Managetti et al. 1998, Weissert et al. 1998) is documented by an expressive positive excursion of values (approximately in the range of 3 ‰) on the high resolution $\delta^{13}C$ curve (Fig.1). $\delta^{13}C$ values in the range of 2,2 to 2,4 ‰ (C1) are characteristic for the upper Barremian to lower Aptian pelagic limestone sequence. They decrease gradually towards the base of the Koňhora Formation (C2: 2.2 -1.7 ‰). Expressive siliciclastic and terrigene organic input was accompanied by changes in nutrient regime and by successive microorganism bioevents (disappearance of nannoconids, Halásová 1999, Michalík et al., 1999). It was connected by decrease in $\delta^{13}C$ value (C3: 1–1, 5 ‰). The first sharper decrease was recorded on the boundary of two cycles, on the top of radiolarite bed. TOC content is low, with strongly oxidised terrestrial organic matter relics. Expressive pyritization appears at the same time. More expressive jump-like increase in $\delta^{13}C$ values (above 3 ‰) in upper part of the second and in the third cycle (Fig.1: C4, C5) denotes the Selli Event. Due to high production of organic matter and relative sediment anoxia, original high TOC content was preserved. Despite of the TOC values in dark and brown grey layers are fluctuating (2.26–0.44–2.71% TOC), the general character of the isotope excursion is continuously rising. Expressive growth of the $\delta^{13}C$ excursion in the third, limestone rich cycle (C6: 3.3 to 3.9 ‰) and mainly in the overlying limestone sequence (C7, C8), where $\delta^{13}C$ values attain 4 to 4.6 ‰, is noteworthy. This positive increase of $\delta^{13}C$ is not accompanied by any more significant accumulation of organic matter (TOC 0.3 to 3%). Detail comparison of lithofacies, geochemical and mineralogical sediment characteristics indicates possible correlation between the positive $\delta^{13}C$ - excursion and a global C-regime disturbance. Raised organics contents resulted from overproduction and from the decay of organics caused rather negative shift in $\delta^{13}C$ values and anoxic environment formed only in some cases.

Lack of correlation between $\delta^{13}C$ changes and those of $\delta^{18}O$ document no significant diagenetic alteration of isotopic ratios. The excursion of $\delta^{18}O$ is shifted towards low values especially in C3 (Fig. 1), signalising compositional (salinity), or carbonate producing water temperature change. This change can be related to a climatic turnover (Michalík et al. 1999).

Conclusion

Comparison of lithofacies, geochemical and mineralogical sedimentary development shows correlation between positive C-event and variations in the C-cycle, evoked by global climatic fluctuations. These changes lasted 2 to 2.4 millions of years. The analysis of the Koňhora Formation in the Rochovica section illustrates the abilities of the C-stratigraphy in the correlation of Tethyan sections.

The Koňhora Formation „anoxia„ was evoked subsequently after change of nutrient regime and overproduction indicated by black shale formation in pale pelagic limestone sequences with locally raised TOC (0.5 to 3 %). Geochemical parameters indicate, that a large part of organic matter has decayed and only slightly disequilibrated the $\delta^{13}C$ ratio of the C oceanic reservoir. The $\delta^{13}C$ value decreased due to overproduction of organic matter and the redox conditions were moved towards the anoxia. However, just the TOC content and the thickness of anoxic beds are relatively small, and expressive increase of $\delta^{13}C$ in the Selli Level can be interpreted as the result of a global climatic change.

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