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Geochemistry of intercalated red and gray pelagic shales from the Mazak Formation of Cenomanian age in Czech Republic

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Pelagic red and gray shales are intercalated within the lower part of the Mazak Formation of Middle Cenomanian age in Czech Republic. A detailed geochemical study of major, trace and rare earth elements and carbon isotopic compositions of organic carbon has been conducted on sixteen red and gray shales. The data suggest that the shales were most likely accumulated in well-oxygenated bottom waters with very limited organic matter supply and consisted of marine organic matter mixed with minor amounts of terrestrial organic matter. The shales were deposited below CCD in one of the tectonic troughs developed along northern margin of the western Tethys. Similar geochemical covariances of major, trace and rare earth elements for the shales suggest palaeoceanographic conditions and provenance during their deposition. The most probable cause for the variation of redox bottom conditions in the mid-Cretaceous deep ocean was periodic changes in the concentration of dissolved oxygen in bottom waters, due to changes in deep water circulation and processes driven climate changes.

Introduction

Cyclicity of multicolored pelagic shales (e.g., red-brown, green gray, black) has been widely recognized in the deep-water sedimentary sequences (Lancelot et al., 1972; Jansa et al., 1979; Arthur, 1979; Dean et al., 1984; 1989; Wortmann et al., 1999). These cycles have been suggested to relate to climatic controls on influx of terrigenous organic matter and sediment, rates of upwelling, productivity, and dissolved oxygen concentration in deep waters (Dean et al., 1984). In particular, the Lower Cretaceous sediments are frequently characterized

by a well-expressed cyclicity (Dean et al., 1978; Jansa et al., 1979; Wortmann et al., 1999). In the deep western Tethys basin most of the middle and late Cretaceous strata were deposited below the carbonate compensation depth (CCD), resulting in carbonate-poor and clay-rich cyclic inter-bedding of red, green, and black shale. The pelagic red clays become the dominant deep sea deposit in western Tethys during the late Cretaceous to early Eocene (Jansa et al., 1979). It is suggested that significant chemical, physical, and mineralogical variations in these pelagic shale sequence may reveal controlling factors influencing the sedimentary environment that is affected by changing chemical, tectonic, oceanographic, and climatic influences (Zhou and Kyte, 1992). However, the origin and significance of the pelagic variegated shale remain a controversy (Lancelot et al., 1972; Vogt, 1972; Dean and Arthur, 1987; Arthur, 1979). A number of studies have focused on the cyclicity of black shales in Earth history, e.g., Wortmann et al. (1999) performed a detailed major-element geochemical analysis of a 3 m long section of cyclically alternating black/green shales of latest Aptian age from the western Tethys. They interpreted the data as indicating periodic changes from a high-productivity and well-oxygenated green shale mode, to a low-productivity oxygen-deficient black shale mode. The detailed study on origin and geochemistry of the cyclically alternating red/green shale is lacking.

In recent years, the study of Cretaceous red-colored pelagic sediments, named as CORB (Cretaceous Oceanic Red Beds), has attracted great attention in the international community, and fundamental changes in the oxidation state, the circulation, and the carbon budget of the ocean during the deposition of these red beds have been suggested (Melinte and Jipa, 2005; Wang et al., 2005; Hu et al., 2005a,b; Neuhuber et al., 2007).

Here, we report a detailed major, trace and rare earth element, and carbon isotope study on a section of variegated shale of Cenomanian age, from the Mazak Formation in Czech Republic. The section is comprised of cyclically alternating red and gray shales. Geochemical study is an attempt to elucidate the cause of color banding of the shales and the palaeoceanographic processes during the deposition of these cyclic multi-colored pelagic deep-sea sediments.

Geological background

In Czech Republic, the Cretaceous strata outcrop at many places in the Carpathian Mountains chain. The most significant Cretaceous area in Czech Republic represents Silesian Unit (outer Western Carpathians) in the Moravskoslezské Beskydy Mts. The geology of the Silesian Unit (Silesian Nappe), and its lithostratigraphy was recently reviewed by Picha et al. (2006). In the Bystry potok near Trojanovice, nearby Frenstat p. R. (Figure 1), an almost continuous, favorably inclined section outcrops, containing pelitic deposits of the Lhoty Formation, comprised of highly bioturbated black shales developed in a Scisti e Fucoidi facies of Albian age. These are overlain by variegated shale strata of the Mazak Formation (Fig.2), which in turn are overlain by the lower part of the Godula Formation. The sequence stratigraphically spans Albian to Campanian. The higher part of the Godula Formation is represented by over 1 km thick sandstone turbidites. The Mazak Formation consists of intercalated red and greenish-light gray shales several centimeters up to 10–20 cm thick (Fig. 3). According to only sporadically occurring dinocysts, the Mazak Formation in the studied section belongs to the upper Middle and the Late Cenomanian.

Detailed profile of red and gray beds within the Mazak Formation of Middle–Late Cenomanian age sampled for geochemical study is

Figure 1. A geological sketch map of the studied area.

Figure 2. Red and gray shales of the Mazak Formation in Czech Republic.

Figure 3. Stratigraphic section of the sampled Mazak Formation in Czech Republic.

shown in Fig.3. Red shales are intercalated with greenish gray shales and rare are thin beds of sandstone turbidite that become frequent higher up the section. A petrographic study of the sampled red and gray shales has shown only minor variations in the quantitative composition of mineral phases present. Main components are quartz, plagioclase, and clay minerals (Table 1). Lack of carbonates and calcareous fossils in the samples indicate their deposition below CCD.

Sampling and analytical methods

Sixteen samples of red and gray shale from the Mazak Formation were collected from a well-exposed outcrop. During sampling, the un-weathered intervals are selected and the weathered parts of the rock have been carefully avoided in the field. In laboratory, the surface layers of rock samples were first cut away, and then these samples have been grinded into small pieces and only fresh portions of rock piece were hand picked, powdered and used for further geochemical study.

Table 1. Estimated typical mineral composition of shales in the Mazak Formation (vol%)

	Red shale	Gray shale
Amorphous part	0±5.4	4.7±6.6
Chlorite	7.24±2.04	7.81±1.8
Illite-smectite or glauconite-smectite	40.6±4.2	53.3±5.7
Plagioclase (albite)	5.78±0.87	4.71±0.87
Quartz	47.07±1.92	29.41±1.56
Hematite	1.24±0.57	0.15±0.22

In this study, we analyzed major, trace and rare earth elements, and TOC concentrations, together with carbon isotopic compositions of TOC, of the red and gray shales from the Czech locality. Major oxide analyses of the shale were performed using X-Ray Fluorescence Spectrometry (XRF). The loss on ignition (LOI) was determined by placing ~1 g of powdered sample into a weighed porcelain crucible and combusting in a furnace at ~1000°C for 4 hrs. After cooling, samples were re-weighed and LOI was calculated from the difference between pre- and post-combustion weights. Samples for XRF analysis were prepared by fusing 0.06g sample with 0.6g silica powder and 7.26g lithium borate ($\text{Li}_2\text{B}_4\text{O}_7\text{:LiBO}_2 = 67\text{:}33$) in a platinum crucible. The fused disks were then analyzed at the Nanjing University using a 9800XP+ X-ray fluorescence spectrometer (made by ARL Corp. of Swiss). The analytical precisions for the oxides are estimated to be <2% for Si and Al, and <5% for other elements based on duplicated analysis of several national reference rock standards. The Fe^{2+} (FeO) and Fe^{3+} (Fe_2O_3) were separately analyzed using a titration method.

The abundance of selected trace and rare earth elements was determined by using ICP-MS method. The shale samples (50 mg) were dissolved using a mixing acid of concentrated HF and HNO_3 (2:1 in volume) in tightly screwed Teflon beakers. After dissolution, the sample solutions were added 1 ml concentrated HNO_3 and dried twice to remove the HF in the samples. The sample solutions were finally dissolved in 2 ml concentrated HNO_3 , and spiked with 10 ppb Rh and made up to 50 ml in 5% HNO_3 solution. These solutions were then measured using a Finnigan HR-ICP-MS at the State Key Laboratory for Mineral Deposits Research in Nanjing University. The analytical precision of trace and rare earth elements is better than 10% based on multiple analysis of a national reference rock standard.

The powdered samples were also analyzed for TOC (total organic carbon) content and $\delta^{13}\text{C}$ TOC using an EA-IRMS (isotope ratio-mass spectrometer) (Finnigan Delta Plus XP coupled with an elemental analyzer) at Nanjing University; reproducibilities were better than ± 0.2 wt% and $\pm 0.1\text{‰}$ for the TOC and $\delta^{13}\text{C}$ TOC, respectively, based on replicate lab standard and sample analyses.

The isotopic compositions were reported in standard delta notation (parts per 1000 or ‰): $\delta^{13}\text{C TOC} = [(R_{\text{sample}}/R_{\text{std}} - 1)] \times 1000$, where $R = {}^{13}\text{C}/{}^{12}\text{C}$.

All the geochemical and isotopic results are listed in Table 2.

Results

Major elements

The studied shale samples are mostly composed of SiO_2 (64.7–69.9 wt%) and Al_2O_3 (13.9–17.6 wt%) with total $\text{SiO}_2 + \text{Al}_2\text{O}_3 > 80$ wt% (Table 2). Other major compositions include Fe_2O_3 (1.86–4.16 wt%), FeO (1.04–2.52 wt%), MgO (1.86–2.08 wt%), K_2O (2.80–3.49 wt%), and Na_2O (0.51–0.86 wt%). The major chemistry of the red and gray shales shows quite similar range of variations, but a significant higher Fe_2O_3 contents are observed for the red shales (Table 2).

The red and gray shale samples show an inverse correlation of silica content with Al_2O_3 and TiO_2 (Figure 4a,b), which may indicate a dilution factor by biogenic silica or quartz to the clay minerals in the shales. An inverse correlation between silica content and Fe_2O_3 is only observed for the red shales (Figure 4c), and we suggest this may reflect a dilution factor of silica to significant hematite

Figure 4. Plots showing correlation between (a) SiO_2 and Al_2O_3 , (b) SiO_2 and TiO_2 , and (c) SiO_2 and Fe_2O_3 .

composition observed in the red shales, whereas hematite occurrence in the gray shales is insignificant (Table 1). A good positive linear relationship exists between Al_2O_3 and K_2O or Na_2O for the gray shales (Figure 5a,b), suggesting a major clay mineral component for the shales.

The major chemical compositions of the red and gray shales are comparable to PAAS (Post-Archean Australian Average Shale; Taylor and McLennan, 1985) and the average upper continental crust values (Rudnick and Gao, 2003), but a depletion by a factor of 4 to 8 in CaO and Na_2O contents are rather significant. The P_2O_5 contents of the red and gray shales are similar (<0.1 wt %) and are lower than PAAS and the upper continental crust (0.15–0.20 wt%).

Trace elements

In general, the trace element concentrations of the red and gray shales are comparable with each other, and they are broadly similar to those of average upper continental crust (Rudnick and Gao, 2003). But a slight depletion in Sr, Zr, Mo, Ba, Hf, and U, and enrichment in Li, Cu, Rb and Cs is observed in both, the red and gray shales (Figure 6).

When compared to the average pelagic clays, (Li and Schoonmaker, 2003), our samples show significant depletion in Mn, Cu, Mo, Ba, and Pb (strong peaks in Figure 7). A slight depletion is also observed for Co, Ni, Sr, Y, and U (Figure 7).

Table 2 Major, trace and rare earth element, and TOC concentrations and carbon isotope compositions of the shales.

	B1	B3	B5	B7	B11	B13	B15	B19	avg.	B2	B4	B6	B8	B12	B14	B16	B20	avg.
SiO ₂ (wt%)	68.1	68.8	69.2	64.7	68.0	68.1	65.1	69.0	67.6	68.4	67.4	68.1	65.3	66.8	69.9	69.0	67.2	67.7
Al ₂ O ₃	14.5	14.0	13.9	16.4	14.9	14.4	15.8	13.9	14.7	15.3	16.3	15.5	17.6	16.6	14.1	15.2	15.4	15.7
TiO ₂	0.53	0.54	0.53	0.61	0.59	0.54	0.62	0.62	0.6	0.60	0.58	0.60	0.67	0.62	0.54	0.62	0.62	0.6
Fe ₂ O ₃	3.37	3.40	3.23	4.09	3.33	3.57	4.16	2.84	3.5	1.86	2.24	1.87	2.02	1.97	2.35	2.34	2.64	2.2
FeO	2.52	2.37	2.34	2.12	2.01	2.30	2.19	1.94	2.2	2.12	1.62	1.86	1.80	1.76	1.44	1.40	1.04	1.6
CaO	0.42	0.40	0.39	0.43	0.44	0.40	0.44	0.52	0.4	0.47	0.44	0.46	0.50	0.44	0.63	0.54	1.18	0.6
MgO	2.08	2.00	1.98	2.08	1.96	2.02	2.08	1.92	2.0	2.00	1.97	1.90	1.98	1.96	1.86	1.88	1.94	1.9
MnO	0.03	0.12	0.12	0.11	0.08	0.03	0.04	0.05	0.1	0.14	0.05	0.15	0.05	0.04	0.30	0.16	0.38	0.2
K ₂ O	2.98	2.98	2.92	3.47	3.32	3.02	3.28	3.02	3.1	3.01	3.21	3.18	3.44	3.24	2.80	3.08	3.25	3.2
Na ₂ O	0.52	0.58	0.56	0.61	0.64	0.54	0.54	0.55	0.6	0.80	0.81	0.75	0.86	0.80	0.63	0.67	0.63	0.7
P ₂ O ₅	0.10	0.08	0.09	0.10	0.10	0.09	0.09	0.09	0.1	0.09	0.07	0.09	0.10	0.09	0.07	0.10	0.10	0.1
LOI	4.34	4.18	3.16	4.82	4.25	4.20	4.71	4.30	4.2	4.43	4.60	4.43	4.81	4.65	4.42	4.38	5.26	4.6
Total	99.57	99.45	98.35	99.50	99.66	99.22	99.04	98.70	99.2	99.17	99.25	98.88	99.11	98.91	99.05	99.35	99.64	99.2
Li (ppm)	39	45	42	48	38	42	49	35	42	45	49	45	49	48	40	42	42	45
Be	1.7	2.0	1.9	2.1	1.8	1.7	2.0	1.9	1.9	2.1	2.2	2.3	2.6	2.3	1.9	2.1	2.3	2.2
Sc	7.6	12	12	14	11	11	13	11	11	13	13	14	15	15	12	13	13	14
V	93	92	88	117	94	92	95	87	95	130	164	115	174	136	111	95	110	129
Cr	72	65	63	74	62	59	72	61	66	68	71	74	80	75	63	72	72	72
Co	23	24	24	22	20	22	21	20	22	21	21	21	22	21	20	18	20	21
Ni	51	54	52	54	49	50	56	47	52	49	58	49	55	53	50	46	52	51
Cu	52	37	51	110	46	43	48	26	52	66	88	65	187	117	27	78	50	85
Zn	72	88	75	75	66	73	73	199	90	108	71	68	71	104	71	67	76	80
Ga	15	16	16	18	15	16	18	16	16	17	20	18	19	18	17	18	19	18
Rb	81	135	130	151	112	114	139	120	123	129	134	144	151	147	123	136	147	139
Sr	48	71	70	88	61	70	77	69	69	82	102	86	95	88	72	78	82	86
Y	12	16	17	19	15	18	16	15	16	19	23	19	21	21	17	18	15	19
Zr	76	78	78	81	77	109	86	133	90	95	145	87	92	113	93	86	86	100
Nb	10	11	11	13	11	14	13	11	12	12	26	13	13	13	13	12	12	14
Mo	0.7	0.6	0.7	0.9	0.7	0.7	0.9	0.5	0.7	0.3	0.2	0.4	0.5	0.3	0.3	0.3	0.4	0.3
Sn	2.8	2.9	2.9	3.6	2.9	2.8	3.4	2.9	3.0	3.2	3.8	3.2	3.4	3.5	3.0	3.1	3.0	3.3
Cs	6.1	9.4	9.4	10.6	7.8	8.4	10.1	8.7	8.8	9.0	9.1	9.9	11	10	9.0	9.6	11	9.8
Ba	240	353	343	392	327	371	343	391	345	387	365	398	399	392	347	356	393	380
Hf	1.5	1.5	1.6	1.7	1.6	1.5	1.7	2.6	1.7	2.1	3.7	1.8	1.9	2.1	1.6	1.7	2.0	2.1
Ta	0.7	0.8	0.7	0.8	0.8	0.6	0.8	0.9	0.8	1.0	1.3	0.9	0.9	1.1	0.8	0.9	1.1	1.0
W	2.9	8.4	2.6	2.8	20	3.1	7.9	2.1	6.3	2.2	1.9	2.2	2.4	2.2	3.8	2.1	2.0	2.3
Pb	24	22	25	27	19	21	25	17	22	17	16	15	340	33	14	18	37	24
Bi	0.4	0.3	0.3	0.6	0.3	0.4	0.4	0.3	0.4	0.4	0.5	0.5	1.2	1.0	0.2	0.4	0.4	0.6
Th	5.5	8.5	8.6	10.3	8.5	8.3	9.7	8.0	8.4	9.8	10.3	10.1	11	11	8.6	9.6	9.2	9.9
U	1.1	1.2	1.2	1.4	1.3	1.2	1.4	1.3	1.3	1.6	1.5	1.6	3.5	2.0	1.4	1.9	1.6	1.9
La	13.8	27.3	26.5	26.8	24.1	25.2	27.5	24.7	24.5	27.2	36.9	28.1	33.3	28.2	26.3	27.6	28.1	29.4
Ce	58.7	67.5	64.9	80.0	58.4	64.1	68.1	51.5	64.1	71.0	104	77.5	94.4	80.5	57.2	68.9	56.7	76.2
Pr	3.13	5.53	5.48	6.49	5.12	5.26	5.98	5.23	5.3	6.25	8.69	6.68	7.97	6.86	5.64	6.60	5.97	6.8
Nd	11.7	20.2	19.5	24.2	18.8	19.3	21.5	19.3	19.3	23.8	32.0	24.7	30.1	25.6	20.5	24.0	21.2	25.2
Sm	2.53	3.62	3.52	4.56	3.63	3.85	3.82	3.62	3.6	4.49	5.45	4.45	5.56	4.82	3.82	4.31	3.34	4.5
Eu	0.56	0.74	0.76	0.98	0.78	0.77	0.80	0.73	0.8	0.90	0.96	0.93	1.09	0.97	0.76	0.86	0.68	0.9
Gd	2.59	3.26	3.33	4.25	3.33	3.80	3.41	3.06	3.4	4.10	4.59	3.98	4.73	4.53	3.47	3.81	2.87	4.0
Tb	0.34	0.41	0.41	0.53	0.42	0.51	0.42	0.40	0.4	0.52	0.62	0.50	0.59	0.55	0.46	0.48	0.36	0.5
Dy	2.22	2.71	2.74	3.36	2.70	3.33	2.76	2.45	2.8	3.23	4.08	3.20	3.77	3.52	3.03	3.07	2.45	3.3
Ho	0.46	0.57	0.58	0.70	0.55	0.68	0.57	0.51	0.6	0.68	0.83	0.67	0.75	0.74	0.62	0.64	0.53	0.7
Er	1.34	1.68	1.74	2.02	1.64	1.93	1.68	1.46	1.7	1.95	2.44	1.96	2.23	2.16	1.85	1.82	1.63	2.0
Tm	0.19	0.25	0.27	0.29	0.24	0.27	0.24	0.21	0.2	0.28	0.34	0.29	0.32	0.32	0.27	0.26	0.25	0.3
Yb	1.22	1.66	1.71	1.89	1.59	1.70	1.58	1.36	1.6	1.94	2.09	1.90	2.00	2.09	1.76	1.72	1.66	1.9
Lu	0.19	0.25	0.26	0.29	0.24	0.25	0.23	0.21	0.2	0.28	0.31	0.28	0.31	0.30	0.26	0.26	0.25	0.3
Ce/Ce*	2.06	1.27	1.24	1.40	1.21	1.28	1.23	1.04	1.3	1.25	1.33	1.30	1.34	1.34	1.08	1.18	1.01	1.2
Eu/Eu*	0.51	0.59	0.61	0.69	0.61	0.58	0.62	0.59	0.6	0.64	0.63	0.67	0.71	0.66	0.59	0.63	0.57	0.6
La _N /Yb _N	0.83	1.22	1.15	1.04	1.12	1.09	1.28	1.34	1.1	1.04	1.30	1.09	1.23	1.00	1.10	1.18	1.25	1.1
Gd _N /Yb _N	1.28	1.19	1.18	1.36	1.27	1.35	1.31	1.36	1.3	1.28	1.33	1.27	1.43	1.31	1.20	1.34	1.05	1.3
TOC (%)	0.04	0.03	0.03	0.03	0.03	0.03	0.04	0.03	0.03	0.04	0.04	0.03	0.03	0.03	0.04	0.03	0.04	0.03
δ ¹³ C (‰)	-26.8	-26.4	-27.4	-26.8	-26.7	-26.7	-27.1	-26.2	-26.8	-27.2	-26.2	-27.0	-26.8	-26.5	-26.4	-26.5	-26.5	-26.6

Note: Ce/Ce* = 2Ce_N/(La_N+Pr_N); Eu/Eu* = Eu_N/(Sm_N+Gd_N)^{0.5}

In particular, the redox-sensitive elements such as V and U are generally lower but Mo concentrations are slightly higher in the red shales (Table 2). There are no significant differences in the Ni contents of the shales (Table 2). The Mn contents in red and gray shales are highly variable from 241 to 967 ppm and 299 to 2966 ppm, respectively, with the latter having slightly higher Mn contents (Table 2). We used the Al-normalized trace element plots, and found no significant correlations between element pairs of V/Al, Mo/Al, U/Al, and Th/Al in both the red and gray shales (Figure 8).

Rare earth elements

We normalized the rare earth elements concentration in our studied shales to the REE concentrations of Post Archean Australian Average Shale (PAAS) compiled by Taylor and McLennan (1985).

Overall, the shale samples in our studied section show similar or slightly lower total rare earth element contents than those of PAAS, and an almost flat PAAS-normalized REE pattern (Figure 9). The red and gray shales display similar flat PAAS-normalized REE patterns with slightly heavy rare earth element (HREE) depletions

Figure 5. Plots showing correlation between (a) Al_2O_3 and K_2O and (b) Al_2O_3 and Na_2O .

($\text{La}_N/\text{Yb}_N = 0.83\text{--}1.34$ and $1.0\text{--}1.30$, and Gd_N/Yb_N ratios = $1.18\text{--}1.36$ and $1.05\text{--}1.43$, respectively). Most of the red and gray shales also show significant positive Ce anomalies with Ce/Ce^* values vary from 1.04 to 2.06 in the red shales, and 1.01–1.34 in the gray shales (Table 2). A negative Eu anomaly is observed for all the shale samples with Eu/Eu^* values of 0.51–0.69 and 0.57–0.71 for the red and gray shales, respectively (Table 2).

Organic carbon contents and carbon isotopic compositions

The red and gray shales show no difference in their total organic carbon (TOC) concentrations and $\delta^{13}\text{C}$ TOC values, which are

Figure 6. Trace element concentrations normalized to the average upper continental crust values (Rudnick and Gao, 2003). (a) red shales, (b) gray shales.

Figure 7. Trace element concentrations normalized to the average pelagic clays (Li and Schoonmaker, 2003). (a) red shales, (b) gray shales.

characterized by extremely low TOC contents of <0.04 wt% with very limited $\delta^{13}\text{C}$ TOC variation from -26.2 to -27.4‰ . In comparison, the Upper Cretaceous interbedded red and green claystones from the DSDP Leg 93 site 603 show higher TOC contents of 0.07 to 0.18 wt%, and 0.08 to 1.14 wt%, respectively, and the green claystones also show heavier $\delta^{13}\text{C}$ TOC values of -24.3 to -26.1‰ (Dean and Arthur, 1987). The TOC concentrations at the top of underlying black shales of the Lhoty Formation vary from 0.3% up to 3.5%.

Discussion

Origins of color banding and their implication

The cycles of multicolored pelagic sediments in deep sea setting is a widespread phenomenon in Earth history. However, the cause for color banding and its implication for palaeoceanographic environment is still a matter of debate. Many researchers suggest that the color is caused by some compound of iron, in particular the relative abundance of the iron ion valence in the silicate structure, the specific bonding of these ions, and hematite is regarded as a pigmenting agent of red shale (Robb, 1949; Velde, 2003; Yamaguchi and Ohmoto, 2006). The source of iron has been suggested to be derived either from submarine hydrothermal venting, or from diagenetic mobilization of iron in pore water. For example, in order to explain the mineralogy and chemistry of the multicolored claystones from DSDP Leg 11 in the western North Atlantic, Lancelot et al. (1972) proposed that volcanic or hydrothermal exhalations superimposed on slow rates of pelagic clay deposition could account for the color banding, mineralogical variations and enrichments of several trace transition elements, such as Mn, Zn, Cu, Pb, Cr, Ni. Vogt (1972) also proposed that the metal content in the Upper Cretaceous claystones was related to increased plume activity in the Atlantic at the time of their deposition. In contrast, the inter-bedding of variegated shale in the Upper Cretaceous of the western Atlantic has been suggested by Arthur (1979) to reflect diagenetic mobilization of redox-sensitive metals

Figure 8. Interelement relationship for the Al-normalized redox-sensitive trace elements in the shales. (a) V/Al-Mo/Al, (b) V/Al-Ni/Al, (c) U/Al-Mo/Al, (d) U/Al-Th/Al.

within anoxic pore waters of the Lower Cretaceous black shales and upward diffusion/advection into the oxidized claystones. Dean and Arthur (1987) suggested a similar mechanism involving upward advection and diffusion of metals from the underlying Middle Cretaceous black carbonaceous claystones for the multicolored claystones of the overlying Upper Cretaceous to lower Tertiary sedimentary sequence at site 603 of DSDP Leg 93.

Through a study of color variability and Mn contents in the multicolored sediments from the Lomonosov Ridge in the central Arctic Ocean, Jakobsson et al. (2000) found that the high MnO

contents are corresponding to the dark to medium brown color banding in the sediment.

These authors also suggested two different processes for the cyclic pattern of color banding and manganese concentration. One is climatic forcing of the transport of source material with large quantities of manganese from northern Siberia during interglacial. The other is relative degree of ventilation of Arctic Ocean waters driven by glacial-interglacial contrasts, which would enhance the precipitation of manganese during interglacials, because of higher bottom water oxygen concentrations. Chemical analysis of the red and gray shales from the Mazak Formation revealed a difference in both the iron and manganese contents. The red shales show higher Fe_2O_3 content (2.84–4.16 wt%) than those of the gray shales (1.86–2.64 wt%). Mineralogically, higher hematite contents are also identified in the red shales (Table 1). However, the Mn concentration shows opposite trend with higher Mn in the gray shales (299–2,362 ppm) than in the red shales (241–967 ppm). Hence, we suggest that the main cause for the color banding in the pelagic sediments of the Mazak Formation is the difference in their ferric iron and hematite concentrations.

Through a study of Precambrian red beds, Yamaguchi and Ohmoto (2006) suggested that red shales are products of oxidizing environments with an adequate supply of Fe^{3+} that is ultimately converted to hematite, the pigmenting agent of red shales, which probably formed *in situ* by oxygenated pore waters during weathering of the source rocks and/or diagenesis of shales. However, if hematite-rich sediments accumulated in sulfate-poor, but anoxic environments, Fe^{3+} -oxides would leach out and gray/green shales would form.

Sedimentary environments for the multicolored shales

Using geochemical proxies, it is possible to trace the redox environments of marine sediments in Earth history (Moffett, 1990,

Figure 9. The PAAS-normalized REE patterns for the shales. (a) red shales, (b) gray shales.

Table 3. Four groups of redox conditions for low calcic shales (after Quinby-Hunt and Wilde, 1996)

Group		I	II	III	IV
		oxic		anoxic	
Fe	(3.75 wt%)	H	H	L	L
Mn	(800 ppm)	H	L	L	L
V	(320 ppm)	L	L	L	H

Note: H - higher; L - lower

1994; Quinby-Hunt and Wilde, 1994, 1996; Yang et al., 2004; Yamaguchi and Ohmoto, 2006). For example, Th/U ratio has been used to infer paleoredox conditions in depositional environments because uranium and thorium behave differently in aqueous environments of different redox conditions. Under oxic conditions, U^{4+} oxidizes to highly soluble U^{6+} , whereas Th^{4+} is not particularly soluble in aqueous solutions and occurs only as Th^{4+} in nature, which led to the geochemical decoupling of U and Th in oxidizing environments. In this study, the red shales show a Th/U ratio of 4.96 to 7.18, while a slight lower Th/U ratio is observed for the gray shales (3.16–6.84). In comparison, the average Th/U ratio of PAAS and the upper continental crust is 3.8 and 3.7, respectively (Taylor and McLennan, 1985). It is suggested that the preferential loss of U over Th probably occurred during diagenesis of the shale. The occurrence of red shales indicated a more oxidized environment that have slightly enhanced U when compared to the gray shales.

Based on Fe, Mn, and V concentrations, Quinby-Hunt and Wilde (1996) proposed four discrete categories of depositional and early diagenetic redox conditions for low calcic shales of $[Ca] < 0.4\%$ (Table 3). Group I shales are characterized by oxic conditions and high Eh with high Mn (>800 ppm, average 1,300 ppm) and Fe (>37,500 ppm, average 56,000 ppm) but low V (<320 ppm, average 130 ppm) concentrations. Fe and Mn are present as insoluble Mn and Fe oxides in this group. Group II shales are deposited under anoxic, nitrate reducing to sulfate reducing conditions at intermediate pH. Mn concentrations are low (<750 ppm, average 310 ppm) owing to its reduction to soluble Mn^{2+} , while Fe may remain bound in oxides or sulfides with concentrations comparable to Group I. Concentration of V in this group is also low (<320 ppm, average 140 ppm).

Group III shales are characterized by anoxic but non-sulfate reducing Eh conditions and intermediate to low pH, which have relatively low Fe (<37,500 ppm, average 23,000 ppm), Mn (<750 ppm, average 170 ppm), and V (<320 ppm, average 170 ppm) concentrations. Group IV shales are characterized by relatively low Fe (<37,500 ppm, average 19,000 ppm) and Mn (<750 ppm, average 76 ppm) but high V (>320 ppm, average 1500 ppm) concentrations, indicating deposition under conditions of high organic matter preservation, suggesting low pH and Eh conditions and possibly conditions favoring methanogenesis (Quinby-Hunt and Wilde, 1994, 1996). On average, the Fe, Mn, V concentrations in the red and gray shales in our studied section suggest they belong to Group I of oxic conditions.

The Ce anomaly in ancient marine sediments is one of the promising tools to trace oceanic redox conditions. A negative Ce anomaly is commonly observed in modern seawater because Ce^{3+} in seawater can be oxidized to insoluble Ce^{4+} and then removed (e.g., Piper, 1974; Elderfield, 1988; Piepgras and Jacobsen, 1992). Moffett (1990, 1994) suggested that this Ce oxidation took place

relatively rapidly in the shallow water environment through bacterial mediation.

Under oxidized conditions, compared to the other REE, Ce is hard to dissolve into water due to insoluble Ce^{4+} . The resulting solution attains a negative Ce anomaly and the residue has a positive Ce anomaly. The hydrogenetic Fe-Mn nodules and crusts usually show a positive Ce anomaly due to oxidative scavenging of Ce by Fe-Mn oxyhydroxides (Pattan and Banakar, 1993; Bau et al., 1996). It is suggested that the REE in Fe-Mn nodules and crusts are derived from oxic seawater that typically shows a pronounced negative Ce anomaly (Elderfield, 1988). In the studied red and gray shales, we suggest that the positive Ce anomaly may indicate an oxic condition during sediment deposition and/or diagenesis. In a plot of Eu/Eu^* and Ce/Ce^* for shales (Figure 10), the gray shales form a linear trend; some of the red shales also plot near this trend, but several samples fall out from this trend with higher Ce/Ce^* values, which provide further evidence for a more oxidized condition for the red shales.

Figure 10. Correlation between Eu/Eu^* and Ce/Ce^* in the shales.

In pelagic sediment, barite is the only sulfate mineral present in abundance, and Ba enrichment has been observed from various settings, such as the Central Indian Basin, the Peru margin upwelling, and the Pacific equatorial divergence. This enrichment generally reflects high biological productivity (Von Breyman et al., 1990, 1992). Although absolute Ba concentration in our studied pelagic shales cannot be used to quantitatively estimate palaeoproductivity, the very low Ba contents (240–399 ppm) in the samples likely imply a low bioproductivity at surface water. Due to the low productivity, the trace elements in the shales are therefore also low, which is in contrast to the high concentrations of trace elements in sediments located in high bioproductivity areas (Brumsack, 1986). The low P contents in our studied shales (below average upper crust value of 742 ppm, Taylor and McLennan, 1985) further points to low nutrient availability during the periods of shale accumulation.

The similar, but extremely low TOC contents (<0.05 wt%) and small variations in $\delta^{13}C$ values of the red and gray shale samples in the studied section (Figure 11) indicate that the sediments were most likely accumulated in an oxygenated water body that probably contained very little organic matter. The carbon isotope compositions of organic carbon (OC) in marine sediments often have been interpreted in terms of the source of the organic matter. Previous studies have shown that Cretaceous marine OC had $\delta^{13}C$ values of about -27 to -29‰ , whereas Cretaceous terrestrial OC had $\delta^{13}C$ values of about -23 to -25‰ (Dean and Arthur, 1987). The carbon isotope study of OC in black claystones from DSDP Hole 603 in the western Atlantic shows a $\delta^{13}C$ range from -24.4 to -26.7‰ , whereas the $\delta^{13}C$ values of OC in DSDP Hole 367 in the eastern North Atlantic

Figure 11. TOC contents and $\delta^{13}\text{C}$ values of the shales.

are ~2 to 3‰ lighter. Dean and Arthur (1987) suggested that at Site 603, the organic matter is largely terrestrial, probably derived from the coastal wetlands of North America that produced extensive Cretaceous coal deposits (Parrish et al., 1982). In contrast, at Site 367, the organic matter is largely marine, derived from accumulations of phytoplankton debris in highly productive shelf and slope environments under strong upwelling conditions that existed along the coast of Northwest Africa in the Cretaceous (Barron, 1985). It is suggested that the organic matter in the marine sediments at Sites 603 and 367 represents two different end-member sources for organic matter in Cretaceous proto-Atlantic Ocean (Dean and Arthur, 1987). Our data ($\delta^{13}\text{C} = -26.2$ to -27.4 ‰) suggest that the OC in the red and gray shales from the Mazak Formation may have been derived from a mixing of terrestrial and marine organic matters in a fairly constant proportion, suggested by the small variation in $\delta^{13}\text{C}$ (Figure 11). The isotope data also indicate that the organic matter was mainly marine, mixed with some terrestrial organic matter and deposited in well-oxygenated bottom waters.

The intercalated red and gray shales in the Mazak Formation of Cenomanian age from the Czech Republic were deposited below CCD in one of the tectonic troughs developed along northern margin of the western Tethys. Our analyses show similar geochemical covariance of major, trace and rare earth elements for both gray and red shales, suggesting similar palaeoceanographic conditions and provenance. Association and variation of major elements (Si, Ti, Al, Fe, Mn, Ca, K, Na, and P), trace elements (Zr, Hf, Sc, Th, Mo, V, Ni, U), and rare earth elements support the interpretation that both the red and gray shales were deposited in an oxygenated, pelagic deep-sea environment, possibly similar to the environments presently accumulating pelagic red clays in the deep basins of the Pacific and Atlantic oceans (Jansa et al., 1979).

We consider it important that our geochemical study of these multicolored shales indicate that the most probable cause for the variation of redox bottom conditions in the mid-Cretaceous deep ocean were periodic changes in the concentration of dissolved oxygen in bottom waters. We can only speculate what such changes could be. They can emanate from changes in the source of the bottom water, or as result of major changes in bottom ocean water circulation, due to changes in basins orography, as the mid-Cretaceous was a period of intensified, global, plate tectonic changes.

The variegated shales of the Mazak Formation are sandwiched between Albian black shales of Scisti e Fucoidi facies below and similar dark gray shales of Turonian age above. The variegated beds do not occur in other parts of the Lower and mid-Cretaceous, thus they do represent, on a broader time scale, a unique paleoceanographic

event. They represent an amalgamation of two different processes. One, which resulted in general increase in oxygenation of bottom waters, and the second one, which drives the cyclic red/green bed alteration. The cause of the first process, as mentioned above, could have been a temporary inflow of more oxygenated bottom waters. However, the alternative hypothesis which should not be discarded is that the sediments oxidation is result of a major decrease in sedimentation rates (Buckley and Cranston, 1988 and references herein). However, as the sediments were deposited below CCD, they lack any calcareous microfossils to allow high biostratigraphic resolution of the age for the strata, to compute sedimentation rates.

The red/green bed cyclicity is of similar scale to that observed on Mesozoic and Cenozoic sediments in the western Tethys, interpreted as resulting from climate changes triggered by the precession of the earth rotation axis (circa 21ka period, Dean et al., 1978; Herbert et al., 1986).

Conclusions

Our geochemical study indicates that the shales from the Mazak Formation in Czech Republic show the following major characteristics:

- 1) The major element chemistry of the red and gray shales shows similar range of variations, with contents of SiO_2 of 64.7–69.9 wt%, Al_2O_3 of 13.9–17.6 wt%, MgO of 1.86–2.08 wt%, K_2O of 2.80–3.49 wt%, and Na_2O of 0.51–0.86 wt%. The red shale shows a significantly higher Fe_2O_3 contents (2.84–4.16 wt%) than those of the gray shales (1.86–2.64 wt%) and contains some amounts of hematite.
- 2) The trace element concentrations of the red and gray shales are comparable with each other, and they are broadly similar to those of average upper continental crust, although a depletion in Sr, Zr, Mo, Ba, Hf, and U, and enrichment in Li, Cu, Rb and Cs are observed in both the red and gray shales. The shales contain low concentrations of the redox-sensitive elements such as Mo, V, Ni, and U.
- 3) The red and gray shales display similar flat PAAS-normalized REE patterns with slightly heavy rare earth element (HREE) depletions ($\text{La}_N/\text{Yb}_N = 0.83$ – 1.34 and 1.0 – 1.30 , and Gd_N/Yb_N ratios = 1.18 – 1.36 and 1.05 – 1.43 , respectively), significant positive Ce anomalies ($\text{Ce}/\text{Ce}^* = 1.04$ to 2.06 in the red shale, and 1.01 – 1.34 in the gray shale), and negative Eu anomalies ($\text{Eu}/\text{Eu}^* = 0.51$ – 0.69 and 0.57 – 0.71).
- 4) The red and gray shales show extremely low TOC contents of <0.04 wt% and a limited range of $\delta^{13}\text{C}$ TOC values from -26.2 to -27.4 ‰. In conclusion, the variegated shales of the Mazak Formation (mid to late Cenomanian) deposited below CCD, in a well-oxygenated bottom waters. Organic matter supply was limited and dominated by organic matter of marine origin, which was mixed with some terrestrial organic matter. Both of these shales were deposited in a similar palaeoceanographic setting and are of similar provenance.

Lack of changes in bioproductivity-sensitive elements suggest, that the occurrence of deep sea oxic deposits is most probably result of periodic increase in dissolved oxygen in bottom waters. We suggest that the inflow of colder bottom waters was triggered by local tectonics, resulting from intrabasinal morphological changes effecting ocean floor.

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