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STABLE CARBON AND OXYGEN ISOTOPES OF SOME CARBONATE-FLUORAPATITES FROM CENOMANIAN AND TURONIAN SEQUENCES, BOHEMIAN CRETACEOUS BASIN, CZECH REPUBLIC

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ABSTRACT

Stable carbon and oxygen isotopes were analysed in the structural CO_3 of carbonate-fluorapatite in phosphate nodules and coprolites present in distinctive horizons at the Cenomanian – Turonian boundary and in late Turonian sequence at the Bohemian Cretaceous Basin of the Czech Republic. The results indicate that the structural CO_3 in the analysed carbonate-fluorapatites is depleted in $\delta^{13}C$ relative to CO_3 in carbonates of comparable age and all samples show negative $\delta^{18}O$ values close to those recorded in mid-Cretaceous carbonate-CO_3. The obtained $\delta^{13}C$ values, however, are higher than those reported in apatite-CO_3 of the late Cretaceous Tythyan upwelling-type phosphates. The $\delta^{13}C$ results are interpreted to indicate that phosphogenesis have taken place in an environment rich in the light isotope of carbon, similar to that usually prevails in the organic-rich pore water below sediment-water interface. The higher $\delta^{13}C$ values in the studied apatites relative to their Tethyan analogues may reflect the signature of the well-documented $\delta^{13}C$ excursion of the Oceanic Anoxic Event 2 at the Cenomanian-Turonian boundary. The $\delta^{18}O$ values suggest paleotemperatures expressive of the mid-Cretaceous climatic warming and a lower paleosalinity than that of normal well-circulated seawater.

Keywords: Stable carbon and oxygen isotopes; OAE 2; Apatite; Cretaceous; Bohemian Basin

INTRODUCTION

The Cenomanian – Turonian boundary is known to have witnessed one of the most expressive global oceanic anoxic events of the Cretaceous; the OAE 2, recognized in Europe, N. America and Asia, including the Czech Republic (Uličný *et al*., 1997) and Iraq (Al-Sheikhly *et al*., 2015). It left its signature as a highly condensed section of organic-rich mudstones and a globally recognized stable carbon isotopic excursion which is believed to represent one of the most extreme carbon cycle perturbations of the

last 100 Myr (Erbacher *et al*., 1996; Jarvis *et al*., 2006; Forster *et al*., 2007). The characteristic $\delta^{13}C$ excursion is found in both carbonates (2.5‰ – 3‰) and organic matter (2.6‰ – 6‰) (e.g. Turgeon and Brumsack, 2006). The $\delta^{13}C$ excursion is believed to have resulted from widespread removal of isotopically light organic carbon into black shales during the OAE 2 leading to ^{13}C enrichment in the oceanic and atmospheric CO_2 reservoirs (Scholle and Arthur 1980; Arthur *et al*., 1988). The rapid fall in the $\delta^{13}C$ at the onset of the Turonian transgression, was explained as a consequence of reworking of the organic matter entrapped in the latest Cenomanian mud rocks, following the eustatic sea-level fall in the latest Cenomanian and its regeneration back to the ocean reservoir, leading therefore, to the waning of $\delta^{13}C$ excursion (Arthur *et al*., 1987; Uličný, 1997).

Oxygen isotopes have been often used to estimate paleotemperature and/ or paleosalinity; both of which are factors controlling oxygen isotope composition in sedimentary carbonates (Longinelli and Nuti 1973; Kolodny *et al*., 1983; Anderson and Arthur, 1983; Steuber, 1999). The $\delta^{18}O$ value increases with increasing salinity; fresh-water carbonates contain an average $\delta^{18}O$ of –8.66‰ and marine carbonates contain an average of –5.25‰ (Keith and Weber, 1964). Moreover, it was noticed that the $\delta^{18}O$ average values increase from older to younger ages from –9.7‰ in the Cambrian to –1.2‰ in the Quaternary carbonates (Keith and Weber, 1964).

Stable carbon and oxygen isotopic composition of CO_3 in carbonate-fluorapatite (CFA) has been studied in various phosphorite deposits in the world, mainly to establish origin and phosphogenic environment (Kolodny and Kaplan, 1970; Al-Bassam, 1977; Al-Bassam, 1980; Shemesh *et al*., 1988; Stolper and Eiler, 2016). The carbon isotope composition of authigenic CFA formed below sediment-water interface, would be enriched in the light isotope of carbon and reflects various organic degradation processes during burial (Curtis 1977; Hudson, 1977). In contrast, the carbon isotopic composition of structural CO_3 in CFA formed by diagenetic phosphatisation of carbonates should be much the same as in the precursor material (McArthur *et al*., 1980). The oxygen isotope composition, on the other hand, should be dominated by that of the seawater or pore water and may be overprinted by various diagenetic processes.

The aims of this paper are to use carbon and oxygen isotopic composition of CO_3 bound to the CFA structure to investigate the phosphogenic environment, origin and

mode of apatite formation at the Cenomanian-Turonian boundary and Late Turonian strata in the Bohemian Cretaceous Basin (BCB). In addition, carbon isotopic composition of the CFA in the phosphate nodules found in black mudstones across the C/T boundary is used here to follow the possible OAE 2 signature in the phosphates, which was reported, as a $\delta^{13}C$ excursion, in organic matter, carbonates and total rock, but not in phosphates. On the other hand, the oxygen isotopic composition of the CFA is used here as a paleotemperature and paleosalinity indicator of water in the environment of apatite formation. The samples are apatite-rich phosphate nodules and coprolites present in distinctive horizons in the Bílá Hora and Teplice formations exposed at Pecínov and Úpohlavy quarries respectively (Fig. 1).

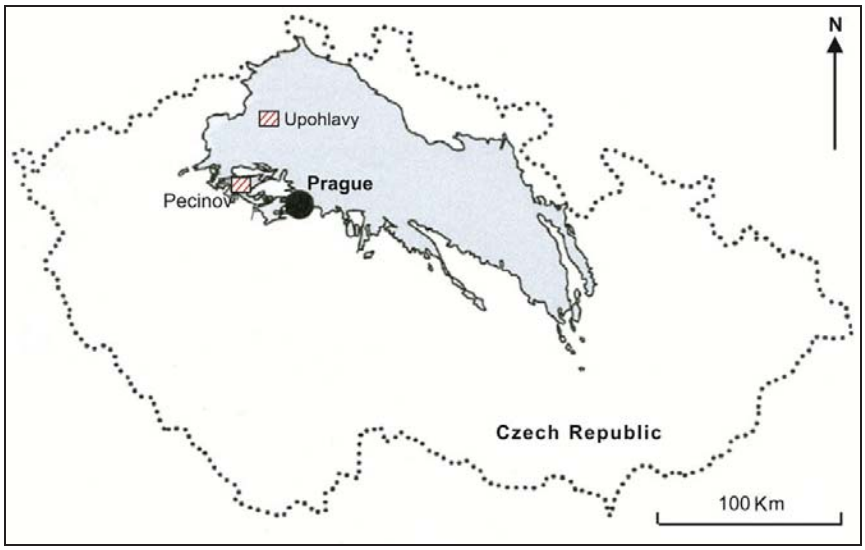


Fig. 1: A sketch map showing the extension of the Bohemian Cretaceous Basin (blue) in the Czech Republic and location of the sampling sites

GEOLOGICAL SETTING

The Cenomanian and Turonian sequences in the BCB have been extensively studied, documented and well dated by various authors (e.g. Čech *et al*., 1980; Uličný *et al*., 1997; Čech *et al*., 2005; Košťák *et al*., in press). The BCB is referred to as an intracontinental basin, formed in the mid-Cretaceous as a seaway between the North Sea and the Tethys Ocean (Uličný, 1997; 2001). It extends in the Czech Republic from Brno in E Moravia across Bohemia to the N and W of Prague (Fig. 1). Sedimentation within the BCB was suggested to have started in the Late Albian or earliest Cenomanian (Valečka and Skoček, 1991). The Cenomanian – Lower Turonian sequence is represented by Peruc-Korycany Formation (Cenomanian) and Bílá Hora Formation

(uppermost Cenomanian – Lower Turonian) (Čech *et al*., 2005; Košťák *et al*., in press). The Peruc-Korycany Formation consists of three members: Peruc and Korycany members (Čech *et al*., 1980) and Pecínov Member (Uličný, 1997). The Upper Turonian sequence is represented by the Jizera and Teplice formations (Čech *et al*., 1980; Wiesse *et al*., 2004). Samples of the present study were collected from the basal part of the Bílá Hora Formation (Pecínov quarry) and the lower coprolitic bed of the Teplice Formation (Úpohlavy quarry) (Figs. 2 and 3).

At the Pecínov quarry the Cenomanian – Turonian boundary is exposed showing the upper part of Pecínov Member and the overlying Bílá Hora Formation. The exposed part of the Pecínov Member includes Parasequences 3 and 4 of Uličný *et al*. (1997). They consist of dark gray glauconitic siltstone and mudstone with pyrite nodules and rare phosphate intraclasts, overlain by the Bílá Hora Formation with an erosive surface (Uličný *et al*., 1997). The lithology of the lowermost part of the Bílá Hora Formation at Pecínov quarry (Unit 1 of Uličný *et al*., 1997) is a dark gray and black highly glauconitic mudstone with abundant brown and gray phosphate nodules; several centimeters in size.

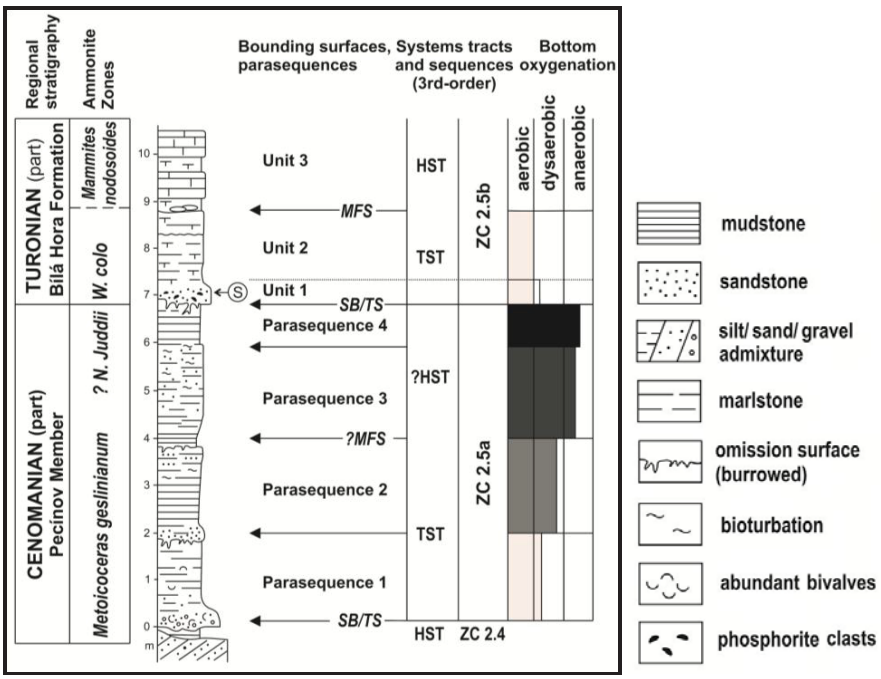


Fig. 2: Lithostratigraphic columnar section of the Cenomanian/ Turonian boundary at Pecínov quarry (modified after Uličný *et al*., 1997) showing sequence boundary surfaces, parasequences, system tracts and bottom oxygenation. TST: transgressive system tract; HST: highstand system tract; MFS: maximum flooding surface; TS: transgressive surface; SB: surface boundary. S: location of phosphate nodules samples 15; 16 and 17

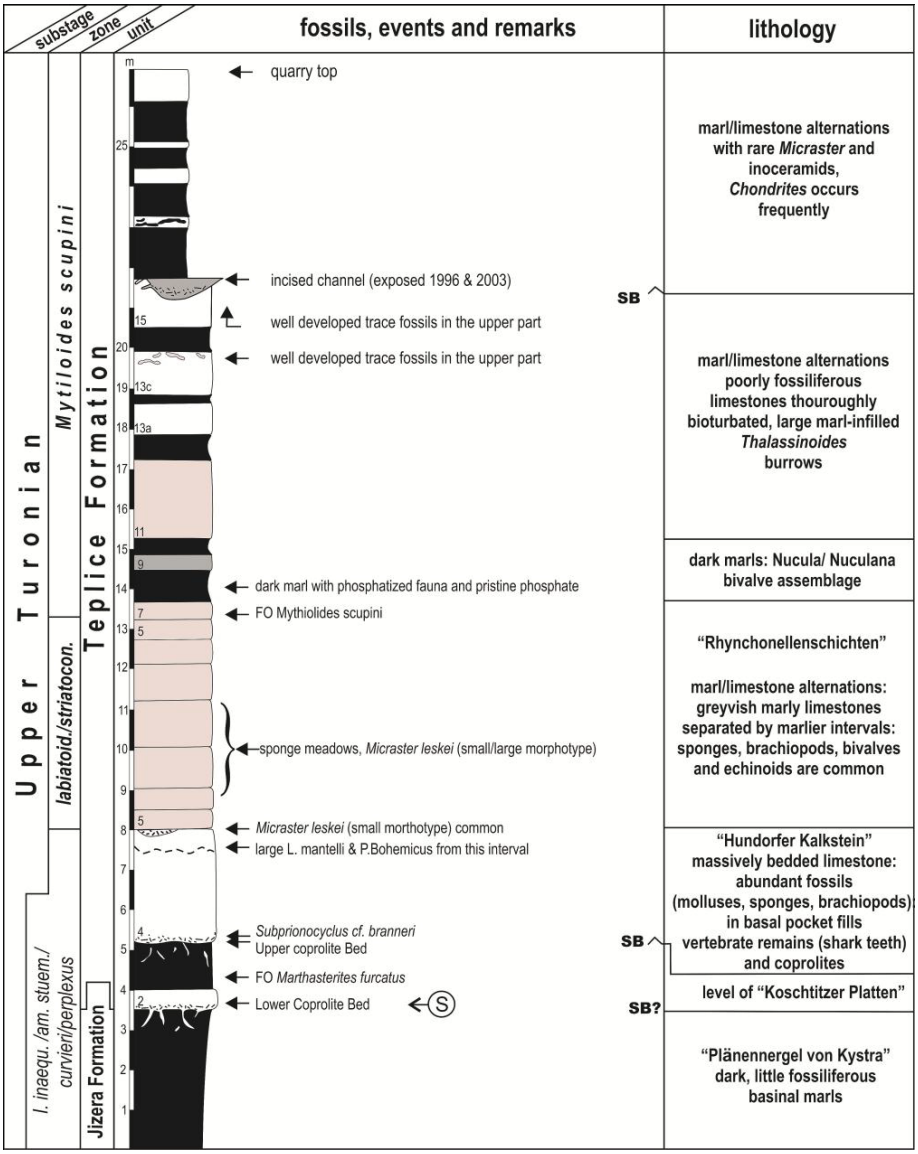


Fig. 3: Lithostratigraphic columnar section of the Upper Turonian sequence at the Úpohlavy quarry showing location of the coprolite beds at the base of Teplice Formation (modified after Wiese *et al*., 2004). SB: surface boundary, S: location of phosphate coprolites samples 39 and 41

At the Úpohlavy quarry two coprolitic beds are recognized in the basal part of the Teplice Formation (Čech *et al*., 1996). The boundary between the Jizera and Teplice formations is taken at the Lower Coprolite Bed which is 20 – 30 cm thick, glauconitic with mm's-size quartz grains, phosphate clasts and coprolites. It grades upward into dark marl, terminated by another erosive surface and topped by the Upper Coprolite Bed (Wiese *et al*., 2004). The coprolites are brown, several centimeters long and about 1cm in diameter.

Phosphates are found in several Cenomanian – Turonian units of the BCB, described in various forms; as nodules, coprolites, sponges and tube-fill deposits. Conspicuous traces of a phosphogenic event occurring at the base of the Bílá Hora Formation (Lower Turonian) were reported from many locations in the southern part of the Bohemian Cretaceous Basin (Žítt and Nekvasilová, 1992; 1996; Žítt *et al.,* 2006). Phosphatisation of precursor materials was reported as the main phosphogenic process of these phosphate components (Žítt *et al*., 1998; Vodrážka, *et al.,* 2009; Žítt *et al.,* 2010).

MATERIALS AND METHODS

Three phosphate nodules from the base of Bílá Hora Formation (the lowermost 0.6 m) at Pecínov quarry (Fig. 2) and two phosphate coprolites from the base of Teplice Formation (lower coprolitic bed) at Úpohlavy quarry (Fig. 3) were analysed for stable carbon and oxygen isotopes. The samples were ground to a fine powder using agate mortar and cleaned from organic matter by H_2O_2 and from carbonate impurities by washing with acetic acid following the procedure of Eagle *et al*. (2010), used by Stolper and Eiler (2016) among other researchers. Carbon and oxygen stable isotopes in CFA structural CO_3 were measured at CGS isotope laboratory, using the method of McCrea (1950). The reproducibility of the analysis is estimated as better than 0.05‰ for both isotopes.

Paleotemperature estimation is based on the equation of Anderson and Arthur (1983):

$$T\,(^{o}C) = 16.0 - 4.14\,(\delta^{18}O_c - \delta^{18}O_{sw}) + 0.13\,(\delta^{18}O_c - \delta^{18}O_{sw})^2$$

Where: $\delta^{18}O_c$ is the $\delta^{18}O$ value (VPDB) of CO_3 in the CFA sample and the $\delta^{18}O_{sw}$ is the selected $\delta^{18}O$ value of the Vienna Standard Mean Ocean Water (VSMOW). The Tethyan Cretaceous Ocean is estimated to range from –1.0‰ to 0.5‰ VSMOW at 34‰ salinity (Steuber, 1999). The seawater $\delta^{18}O$ value used in this estimation is (–1.0‰ VSMOW) according to previous isotope work on the Cenomanian and Turonian rudists of the BCB (El-Shazly *et al*., 2011). Salinity (‰) estimation was calculated using the equation of Buening and Spero (1996):

$$\delta^{18}O_{sw} = 0.39 \text{ X } salinity - 13.46$$

All samples were analysed by X-ray diffractometry (CGS laboratories); the powder X-ray diffraction patterns of whole-rock samples were collected on a Bruker D8

Advance diffractometer, using Cu*K*α radiation (Fig. 4). Structural CO_3 content in CFA was estimated (as CO_2 wt.%) from the XRD diffractograms (Table 1) following Gulbrandsen (1970) equation:

$$Y = 23.634 - 14.7361X$$

Where: $Y = CO_2\%$ and X = delta 2 Theta (*hkl* 410 and *hkl* 004).

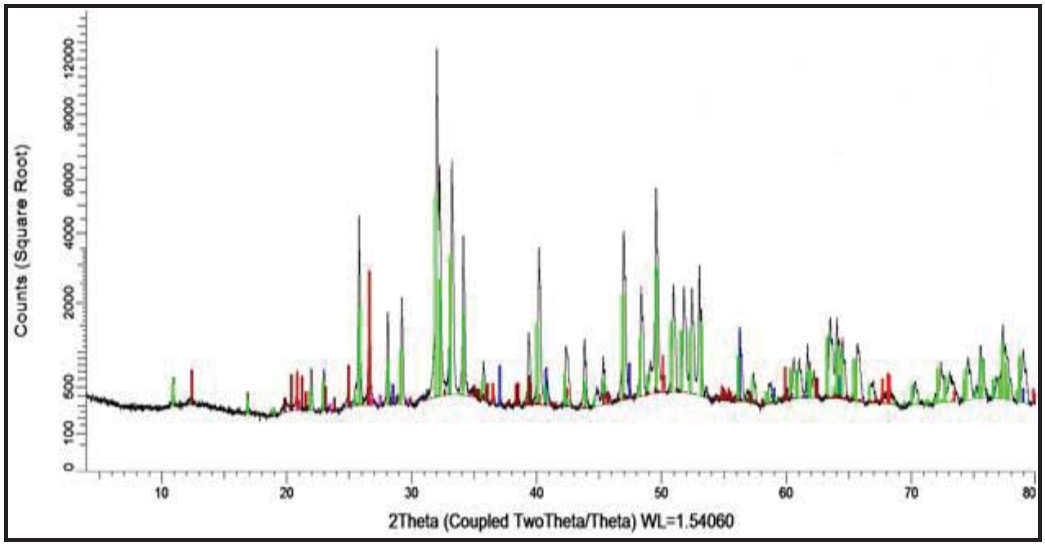


Fig. 4: X-ray diffractogram of a phosphate nodule (sample 16) after purification from organic matter and carbonate impurities showing almost pure CFA spectra (green) with traces of quartz, feldspar, kaolinite and pyrite

Table 1: Carbon and oxygen stable isotopes and CO_2 content of carbonate-fluorapatites

Sample no.	CO_2 (wt.%)	$\delta^{13}C$ (‰ VPDB)	$\delta^{18}O$ (‰ VPDB)	$\delta^{18}O$ (‰ VSMOW)
15 (nodule)	5.49	-0.86	-5.13	25.63
15 (repeated)	5.49	-0.98	-5.26	25.49
16 (nodule)	5.10	-1.23	-4.90	25.86
17 (nodule)	5.36	-1.08	-4.86	25.91
39 (coprolite)	5.51	-1.83	-4.94	25.82
41 (coprolite)	5.58	-1.68	-4.72	26.05

RESULTS

The stable carbon and oxygen isotope results are shown in Table 1 together with structural CO_3 content (expressed as CO_2 wt.%) in the CFA, derived from the X-ray diffraction spectra of the purified phosphate components (Fig. 4). The CO_2 content varied from 5.10 wt.% to 5.58 wt.%; slightly higher values were observed in the coprolites samples. The $\delta^{13}C$ ranged from –0.69‰ to –1.83‰; the apatite-CO_3 in the

coprolites is higher in the light isotope of carbon relative to that in the nodules. The results of oxygen isotope analysis show depleted $\delta^{18}O$ values in all samples. They range from –4.72‰ to –5.26‰ with minor variations between nodules and coprolites. Paleotemperature estimations, based on oxygen isotopes, showed 33.9 – 36.0 °C for the phosphate nodules and 33.2 – 34.3 °C for the phosphate coprolites. Paleosalinity estimations showed values ranging from 21.0 to 22.4‰.

DISCUSSION

Carbon isotopes

Comparison with carbonates: The present carbon isotope results ($\delta^{13}C$ values ranging from –0.69‰ to –1.83‰) indicate significant enrichment of ^{12}C in the structural CO_3^{2-} of the CFA in the phosphate nodules and coprolites (represented by low $\delta^{13}C$ values) relative to carbonates of comparable age. The results, however, fall within the grand range of normal marine limestone (Veizer and Hoefs, 1976). In view of the decreasing trend of $\delta^{13}C$ in marine carbonates noticed with increasing age (Veizer and Hoefs, 1976) and using their narrow range estimate; the $\delta^{13}C$ for the C/T marine carbonates (92 Myr) should be around +2.2‰ (VPDB), considering normal marine conditions. This is higher than the $\delta^{13}C$ reported in this work for the CO_3 in the apatite structure by about 3‰ to 4‰ (PDB) indicating a source of carbon other than that of well-circulated seawater.

This discrepancy is confirmed by the higher $\delta^{13}C$ values reported in calcite-CO_3^{2-} of Cenomanian and Turonian marine carbonates in the BCB and elsewhere in Europe (Erbacher *et al*., 1996; Uličný *et al*., 1997; Wiese *et al*., 2004; Jarvis *et al*., 2006, Forster *et al*., 2007; El-Shazly *et al*., 2011). Higher $\delta^{13}C$ values were found in rudist's carbonates of Cenomanian and Turonian age from the BCB, reported to range from –0.61 to +4.52‰ (VPDB) in the former and from +3.06‰ to +3.19‰ (VPDB) in the latter (El-Shazly *et al*., 2011). The relatively higher $\delta^{13}C$ values are also found in the late Turonian limestones directly underlying the Lower Coprolite Bed at the base of the Teplice Formation; reported by Wiese *et al*. (2004) to have elevated $\delta^{13}C$ values at 1.4‰ to 1.7‰, increasing up to 2.4‰ in the carbonates enclosing the Coprolite Bed.

Comparison with other phosphates: The $\delta^{13}C$ values reported in this work are higher than those found in carbonate-fluorapatite formed in the late Cretaceous upwelling phosphogenic systems of the Tethys Ocean. The $\delta^{13}C$ isotopic values in the latter apatites were reported to range from –5.7 to –8.69‰ (Kolodny and Kaplan 1970;

Al-Bassam, 1980; McArthur *et al*., 1980, Shemesh *et al*., 1988; Stolper and Elker, 2016). Such differences may be partly explained by the younger age and different phosphogenic systems of the Tethyan phosphorites. It is well known that phosphogenesis in the Cenomanian – Turonian sequence of the BCB did not take place and was not influenced by upwelling sedimentary regimes and the process was a consequence of sequence condensation and starvation accompanied by an abnormal burial of organic matter.

Source of carbon: The enrichment of the light isotope of carbon in the apatite-CO_3, demonstrated in the present work, compared to that in calcite-CO_3 of comparable age can only indicate that the carbon in the apatite-CO_3 was derived from the dissociation of organic matter during phosphate precipitation (Anderson and Arthur, 1983). The light isotope of carbon may have been supplied by the biochemical disintegration of P-rich organic matter, taking place in the interstitial pore water below sediment-water interface. Organic matter is considered the main source of light carbon isotope in sedimentary carbonates (Jarvis *et al*., 2006). The general depletion of $\delta^{13}C$ in the marine sedimentary apatites appears to be a general case (Kolodny and Kaplan 1970; Al-Bassam, 1980; McArthur *et al*., 1980, Shemesh *et al*., 1988; Stolper and Elker, 2016).

Genetic implications: Phosphatisation of carbonates has been often assumed as a phosphogenic process of the Cenomanian-Turonian phosphate components (Žítt *et al*., 1998; Vodrážka *et al*., 2009; Žítt *et al*., 2010). However, the lower $\delta^{13}C$ values in the CFA of the phosphate nodules studied relative to those in open marine carbonates of the same age, may furnish evidence that phosphatisation of carbonate precursors (replacement of carbonate by phosphate) should be excluded as a major phosphogenic process of the phosphate nodules. Otherwise, they should have inherited the heavier carbon isotopic composition of the carbonate precursor (McArthur *et al*., 1980). Moreover, neither the Pecínov Member nor the basal part of Bílá Hora Formation in the Pecínov quarry contain any authigenic carbonates; they are carbonate-deficient, glauconitic siliciclasts.

The OAE 2 signature: Carbon isotopic analysis of Cenomanian – Turonian carbonates shows positive excursion of $\delta^{13}C$ at or very close to the C/T Boundary. The peak

positive excursion in the sequence is estimated by 3.7‰; lowered to 2.8‰ in the earliest Turonian and in the latest Cenomanian (Erbacher *et al*., 1996). The positive excursion is also demonstrated in the $\delta^{13}C$ of organic matter, the magnitude of which was estimated by more than 4‰. It was considered by Uličný *et al*. (1997) as comparable to the values recorded in North America and Northern Africa and led him to suggest that it was controlled by a global paleoceanographic mechanism and a signature of intensive burial of organic matter at the OAE 2.

The relatively higher $\delta^{13}C$ values recorded in the apatite-CO_3 of the phosphate nodules present at the C/T boundary in the BCB, compared to their Campanian-Maastrichtian Tethyan analogues, may be linked, in addition to the other factors discussed above, to the positive $\delta^{13}C$ excursion recorded in carbonates and organic matter at the C/T boundary interval. Much higher content of the heavy isotope of carbon was reported in C/T boundary carbonates, relative to other carbonates of the sequence; considered by Turgeon and Brumsack, (2006) as the signature of the OAE 2. The same phenomena could explain the higher $\delta^{13}C$ values in the phosphate coprolites of late Turonian age relative to other Cretaceous marine sedimentary apatites. A positive excursion in the $\delta^{13}C$ was recorded in the carbonates embracing the coprolites-bearing beds and was related to a minor oceanic anoxic event (Wiese *et al*., 2004). However, in view of the limited number of samples analysed here and the wide range of carbon isotopic data recorded in the marine apatite-CO_3 of the world, such suggestion cannot be verified.

Oxygen isotopes

Comparison with other phosphates and carbonates: Stable oxygen isotope composition of phosphates and carbonates is a reflection of that in water where they were precipitated. It is highly influenced by salinity and temperature of the water (Anderson and Arthur, 1983; Buening and Spero, 1996; Andreasson *et al*., 1996) and consequently by water depth (Ando *et al*., 2010). The $\delta^{18}O$ found in the studied apatites show depleted $\delta^{18}O$ values in all samples; ranging from –4.72 to –5.26‰ (VPDB) and are comparable in this respect to the lower limits of values reported for $\delta^{18}O$ in the structural CO_3 of CFA in the late Cretaceous phosphorites of lower latitudes in the Tethys Ocean. The latter was reported to range from –5.1 to –9.9 ‰ (Kolodny and Kaplan, 1970; Al-Bassam, 1980; Shemesh *et al*., 1988; Stolper and Eilker, 2016).

The present results of oxygen isotopes in the apatite-CO_3 are close to the values reported for carbonates of the same age. It was reported that the $\delta^{18}O$ values tend to decrease with increasing age (Veizer and Hoefs, 1976). Using their estimates, the $\delta^{18}O$ for a 92Myr old carbonates is estimated to be –3.5‰ (VPDB). The $\delta^{18}O$ values reported for carbonates in rudists of Cenomanian and Turonian age in the BCB showed values ranging from –6.61‰ to –2.93‰ for the Cenomanian samples and –5.01‰ to –4.67‰ for the Turonian samples (El-Shazly *et al*., 2011). The $\delta^{18}O$ in the Jizera Formation, as reported for total rock samples by Wiese *et al*. (2004), fluctuates around –4.5‰, but increases sharply by 1.5‰ at the base of the Teplice Formation, reaching a maximum of 3‰ in the carbonates bordering the coprolite beds and marking a significant positive shift of $\delta^{18}O$ in these carbonates. This shift was explained by Wiese *et al*. (2004) to reflect a cooling event induced by Boreal currents, but this was not noticed in the apatite-CO_3 of the coprolites studied.

Estimation of paleosalinity and paleotemperature: The $\delta^{18}O$ values obtained in the present study indicate a lower water salinity of 21.0 – 22.4‰ compared to normal seawater salinity of about 34‰, suggesting that these apatites did not form in open well-circulated seawater, but in a lower salinity environment. The water salinity estimates, conform to a semi-closed phosphogenic microenvironment below sediment-water interface. Salinity of the interstitial P-rich waters may be significantly lower than the overlying well-circulated seawater due to the biochemical degradation processes of organic matter (e.g. Glenn and Arthur, 1990).

The paleotemperature estimates obtained in this study are close to those found in the carbonates of Cenomanian and Turonian rudists in the BCB, developed in a well-circulated seawater (El-Shazly *et al*., 2011) and are comparable to estimates reported in sequences elsewhere (Jarvis *et al*., 2006; Forster *et al*., 2007), indicating much warmer temperatures than today. Paleotemperature estimation in this study showed 33.9 – 36.0 °C for the phosphate nodules (latest Cenomania – earliest Turonian) and 33.2 – 34.3 °C for the phosphate coprolites (Late Turonian). El-Shazly *et al*. (2011) reported mean seawater paleotemperatures ranging from 34.7 °C mean value for Cenomanian rudists and 33.8 °C for Turonian rudists analysed in the BCB sequences.

Warm temperatures are typical of the mid-Cretaceous which was a time of intensive greenhouse conditions, with surface and deep water temperatures much higher than

today, high sea-level, low latitudinal temperature gradients and absence of ice sheets (Schlanger and Jenkyns, 1976; Haq *et al*., 1987; Clarke and Jenkyns, 1999; Huber *et al*., 2002; Wilson *et al*., 2002; Moriya *et al*., 2007; Friedrich *et al*., 2008). Following the Cenomanian warming, peak tropical surface temperatures in the range of 32 °C to 37 °C have been recorded from the earliest Turonian (Huber *et al*., 2002; Norris *et al*., 2002; Wilson *et al*., 2002). At the C/T boundary these high temperatures were associated with rapid accumulation of organic carbon-rich sediments of the OAE-2 (Schlanger and Jenkyns, 1976).

However, conclusions regarding paleosalinity and paleotemperature, based on oxygen isotopes ($\delta^{18}O$), should be considered cautiously in view of the problems that may face such estimation. Depth of the environment could influence the oxygen isotopic composition (Ando *et al.,* 2010) and the diagenetic exchange of oxygen isotopes with normal marine water during reworking of the phosphate components and with meteoric water after emergence of the sequence might have partially changed the original oxygen isotopic composition.

CONCLUSIONS

The enrichment in the light isotope of carbon in the apatite-CO_3 compared to calcite-CO_3 of comparable age indicates that the phosphogenic environment was rich in carbon derived from light carbon source which can be furnished by the dissociation of organic matter. These results provide evidence that phosphatisation of carbonates was not a major phosphogenic process in the formation of phosphate nodules and phosphate coprolites. Otherwise they should have inherited the carbon isotopic composition of the carbonate precursor

In the case of phosphate nodules, the relative enrichment in the heavy isotope of carbon in apatite-CO_3 relative to upwelling analogues could be related to the well documented positive $\delta^{13}C$ excursion recorded in the associated carbonates and organic matter in the BCB and elsewhere in Europe and the world. The same may be valid in the case of phosphate coprolites, where a positive $\delta^{13}C$ excursion left its signature in the carbonates embracing the coprolites-bearing beds.

The oxygen isotopes in the apatite-CO_3 indicate that these apatites were formed from lower salinity water than open well circulated seawater. Such environment may

have been available in the pore and interstitial phosphorus-rich water below sediments-water interface, where phosphogenesis seems to have occurred.

The $\delta^{18}O$ values of the Late Cenomanian-Early Turonian phosphate nodules and the Late Turonian phosphate coprolites are close to temperatures estimated for the carbonates in rudists of both ages in the BCB and comparable sequences elsewhere indicating much warmer temperatures than today, but this estimation may be also influenced by the variable salinity of the environment, depth and diagenetic modifications.

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