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A PRELIMINARY INVESTIGATION INTO THE CARBON ISOTOPE STRATIGRAPHY AND THE OCEANIC ANOXIC EVENTS RECORDED IN THE APTIAN – ALBIAN PLATFORM CARBONATES OF PĂDUREA CRAIULUI, APUSENI MOUNTAINS (ROMANIA)

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Abstract: Whole rock carbonates samples from the Aptian to Middle Albian deposits of the Pădurea Craiului Mountains were analysed for carbon and oxygen isotopes. The data defines the first continuous stable isotope baseline trends of the Early Cretaceous in the Western Romanian Carpathians (Apuseni Mountains). During the Late Jurassic to the Late Cretaceous Pădurea Craiului was part of a larger carbonate-platform belt which developed in the Thetyan region. The isotope data provides opportunities to recognize the presence of two major $\delta^{13}C$ positive excursions that have been attributed to the OAE1a (upper part of Ecleja Formation and Valea Măgurii Formation) and 1b (Vârciorog Formation – Subpiatră Member). From a background of 2 – 3‰, a significant $\delta^{13}C$ negative excursion to values as low as 0.46‰ has been recorded in the early Aptian preceding the OAE1a. A second major $\delta^{13}C$ negative (0.74 ‰) excursion was found in the shale deposits of the basal part of the Vârciorog Formation (Late Aptian) and has been assigned to the Fallot major $\delta^{13}C$ perturbation. The lower part of the Subpiatră limestones (Late Aptian – Albian) are characterized by lower $\delta^{13}C$ values (from 2.95 to 2.97‰) as compared with the values recorded in their upper part (from 3.75 to 4.70‰). Such a considerable increase of the $\delta^{13}C$ values from 2.95‰ to 4.70‰, followed by a small drop down to 3.75‰, and then another increase up to 4.23‰ is characteristic to the OAE1b. Large fluctuations of $\delta^{18}O$ values between -2.37 and -9.58 ‰ suggest a warming episode during Early Aptian followed by a cooling trend in the latest Aptian-Early Albian.

Keywords: C-isotopes, carbonates, Early Cretaceous, oceanic anoxic events, Pădurea Craiului, Apuseni Mountains

1. INTRODUCTION

The deposits which out crop in the Pădurea Craiului Mountains are part of a larger carbonate-platform belt developed during Late Jurassic to Late Cretaceous in the Tethyan region. The present work is the first C- and O-isotope stratigraphic study performed on the Early Cretaceous carbonate rocks from Pădurea Craiului. Our data allowed us to perform regional stratigraphic correlations, and to identify major perturbations of the carbon cycle associated with oceanic anoxic events.

In recent years, the interest in Cretaceous climate has been renewed with the goal of better constraining the controls on climate change during intervals of overall warmth. Through the Late Jurassic to Late Cretaceous, high resolution composite carbon and oxygen isotope curves have been published, covering parts of the northern Tethyan continental margin and today cropping out in the northern Alps, southern Italy and Adriatic platform (Jenkyns, 1991; Jenkyns, 1995; Davey& Jenkyns, 1999; Luciani et al., 2001; Weissert&Erba, 2004; Luciani et al., 2004). The Mid- to Late Cretaceous is characterized by a repeated occurrence of quasi-global deposition of organic-rich sediments (black shale). These short-lived (~0.5-1 My) events are referred to as the Oceanic Anoxic Events (OAEs). Such events occurred in the early Aptian (~120.5 Ma; OAE1a), across the Aptian/Albian boundary (~113-109 Ma; OAE1b), in the early Late Albian (~101 Ma; OAE1c), in the latest Albian (~99.5 Ma; OAE1d), across the Cenomanian-Turonian boundary (~93.5 Ma; OAE2), and in the

Coniacian-Santonian (~86-85 Ma; OAE3). During the anoxic events, rapid and extreme warming and subsequent rapid cooling have been suggested by geochemical proxies (Foster et al., 2007). Thus, an OAE is considered to be undertaken as a role of the thermostat in the greenhouse world through eliminating the carbon from the atmosphere (i.e., CO_2) into the carbonaceous sediment as black shale (Weissert & Erba, 2004). Forcing of this climate transition is ascribed to massive eruption of Large Igneous Provinces (LIPs) and associated CO_2 input into the atmosphere (Snow et al., 2005; Kuroda et al., 2007). Although the possible relationships between LIPs activities and OAEs have been described (e.g. Weissert & Erba, 2004; Keller, 2008), detailed processes and causal mechanisms of these distinct events are controversial.

Isotope studies represent a major tool in understanding the causes of Cretaceous OAEs (Jenkyns, 2003). In addition to the widespread distribution of organic carbon-rich sediments, OAEs are also characterized by low abundances or absence of benthic foraminifera and concomitant positive $\delta^{13}C$ excursion. These features have been collectively explained by extensive (ocean-wide) water-column stratification, bottom water anoxia, increased primary production and/or burial of isotopically light organic matter, and probably a resultant draw-down of atmospheric CO_2 (Föllmi et al., 2006).

Among the many black-shale horizons identified on land and in the oceans, the Selli Event (OAE1a) and Bonarelli Event (OAE2) have been established to be of global distribution (e. g. Luciani et al., 2001; Takashima et al., 2006; Keller, 2008). Although Mesozoic sediments recording OAEs, typically display positive carbon isotope excursions, bulk inorganic and organic carbon isotope records of the OAE1a and OAE2 oceanic anoxic events commonly also show a relatively rapid negative shift, which appears to be worldwide and therefore must indicate a perturbation of the global carbon cycle. Several mechanisms have been proposed to explain these negative $\delta^{13}C$ excursions (van Breugel, 2006, and literature therein): (1) recycling of respired CO_2 in stratified seas (Küspert, 1982; Schouten et al., 2000); (2) massive release of methane from gas hydrates (Dickens et al., 1995; Hesselbo et al., 2000; Kemp et al., 2005); (3) thermal release of methane from organic carbon-rich strata by intruded magmas (Svensen et al., 2004; McElwain et al., 2005); (4) combustion of terrestrial carbon deposits accumulated in swamps (Kurtz et al., 2003); (5) asteroid or comet impacts (Glikson, 2005).

2. GEOLOGICAL BACKGROUND

The Pădurea Craiului Massif is situated in the northwestern part of the Apuseni Mountains (Western Romanian Carpathians) (Fig. 1). It was mainly shaped through the sedimentation processes and the tectonic phases associated to Alpine orogenesis. Most of its formations belong to the Bihor tectonic unit and some formations belonging to the Codru Nappe System can be identified on narrow areas in the south and southwest (Ianovici et al., 1976; Săndulescu 1984).

The basement is made up of crystalline schists of the meso-metamorphic Someş Series with sedimentation started during the Permian with detritic deposits interbedded with rhyolites. The overlying Triassic deposits are unconformable and include detritic formations (Early Triassic) and massive layers of carbonate rocks (Middle Triassic). During the Kimmeric tectonic phase the region is uplifted and consequently the Late Triassic is absent.

The Early Jurrasic deposits have a thickness of about 200 m and include: (1) the detritic formation (Hettangian – Early Sinemurian) in Gresten facies composed of a red breccia – conglomerates – sandstone member and a clay – marl member, (2) the limestone formation (Late Sinemurian – Pliensbachian) that comprises the limestone with Griphaea member and the limestone with cherts member, and (3) the marl formation with ammonites and belemnites (Toarcian).

The Middle Jurassic deposits seldom go beyond a thickness of approximately 10 m and they consist of marls for the most part. The Late Jurassic formations are massive (over 100 m thick) and are made up exclusively of limestone. During Late Jurassic and Early Cretaceous the limestone deposits have been uplifted and resulted in a paleo-karst surface that hosts discontinuous bauxite deposits. Early Cretaceous sedimentation started with the deposition of fresh-water limestones (Hauterivian) followed by successive layers of marine limestones (Barremian), marls (Aptian), marine limestones (Aptian), glauconitic sandstone (Aptian-Albian) and ended with a package of red detritic deposits (Cenomanian – Turonian).

The geological formations younger than the nappes from the Pădurea Craiului Mountains are the sediments of the Late Cretaceous, the Banatitic rock bodies, the Sarmatian sediments, the Oarzăna gravel, and the Quaternary deposits. The sediments of the Late Cretaceous formations crop out in several isolated areas out of which the most extended is the Rosia Basin. They consist of three major formations: the lower formation with sandstones and conglomerates (Coniacian), sandstone and marls in the middle part (Early Santonian – basis of Late Santonian), and the upper marl formation (Late Santonian – Campanian).

Following positive epirogenetic movements and two main phases of magmatic activity (Late Cretaceous – Paleocene and Badenian – Pliocene) completed the morphogenesis of the Pădurea Craiului Mountains and the formation of the Pannonian basin to the east. The Late Cretaceous Banatitic magmatism (Berza et al., 1998) consists of several shallow intrusive bodies (rhyolites, rhyodacites and granodiorites) that occur on the southern flank of the Pădurea Craiului Mountains. The Sarmatian sediments occur as transgressive and unconformable patches over the Early Cretaceous deposits and consist mainly of pelitic rocks. Thick deposits of sandy clays in which poorly sorted blocks and fragments of clasts are included occur on many high areas of the Pădurea Craiului Mountains. They are known as the Oarzăna gravel. The Quaternary deposits comprise alluvium, fans of torrential bodies, debris at the bottom of steep slopes, soils and residual deposits, and travertine precipitated from karst waters.

3. SAMPLING

For the present study we have sampled Early Aptian successive layers of shales (Ecleja Roşiorului Hill and Vasii Valley) and marine limestones (Bobdei Valley) belonging to Ecleja Formation, Late Aptian marine limestones belonging to Valea Măgurii Formation (Măgurii Valley), and Late Aptian-Albian succession of limestones with rudists belonging to Subpiatră Member of the Vârciorog Formation (Subpiatră Quarry – Recea Valley) (Table 1).

The Ecleja Formation was first described by Patrulius et al., (1968) and consists of a package of marls and marl siltites, 700-800 m in thick, with an intercalation of organoclastic limestone at the base of the formation. The Bobdei Valley limestone member (nomen novum – Cociuba, 1995) is a succession of gray or dark grey limestone, stratified in metrical banks, with orbitolinids, lenticulins, echinid fragments, and sometimes with terigen material (quartz fragments). The bottom and the upper part include some metrical banks of shales as well. The limestone belonging to this member outcrops in the Bobdei Valley, where both the upper and the lower limits of the formation can be found. The limestone develops on a thickness of about 40 m. The foraminifer and algae assemblage includes: *Palorbitolina lenticularis*, *Sabaudia capitata*, *Voloshinoides n. sp*., *Orbitolinopsis pygmaea*, *Netrocholina*, and *Paracoskinolina*. The asseamblage is characteristic for the Early Aptian.

The Valea Măgurii Formation represents a succession of gray and light gray limestones, stratified in metrical banks, generally fine micritic, but also pelmicrosparitic, with orbitolinids and rudists, lying on the marls belonging to the Ecleja Formation. The lower part of the formation is very poor in microfossils and lighter in colour as well. The upper part contains more fossils, being dominated by biopelsparites and biopelmicrosparites with foraminifera and rare algae, out of which we can mention: *Orbitolinopsis cuvilieri, Orbitolinopsis buccifer, Orbitolinopsis pygmaea, Palorbitolina lenticularis, Dervantina filipescui, Nautiloculina bronnimanni, Archaeoalveolina reicheli, Neotrocholina sp., Salpingoporella muehlbergii, Salpingoporella n. sp. 1, Pseudoactinoporella fragilis, Carpathoporella fontis*. This assemblage is exclusively Bedoulian in age and includes many species that can also be found in the Valea Bobdei Member. The only species that we identified being exclusively related to the Valea Măgurii Formation is *Pseudonummoloculina aurigerica* (Cociuba, 2000).

The Vârciorog Formation is defined as a succession of gray to black marls, marly and glauconitic sandstone and gray to black limestone with orbitolinids and rudists, discordantly covering a slightly unlevelled paleorelief developed on the Valea Măgurii limestone, where small iron-bauxite gatherings are also found. The entire succession is 400 to 500 m in thickness. In some areas a subaerial slide breccia occurs. It consists of large Jurassic and Cretaceous limestone blocks and even of some bauxite randomly or compactly disposed, cemented with sparitic calcite and red siltic material. It is known as Gugu Breccia (Patrulius et al., 1968). The limestone intercalations of the Subpiatră Quarry display a typical carbonate platform facies (Daoud et al., 2004; Bucur et al., 2010). The total thickness of the Late Aptian – Middle Albian limestones in the Subpiatră Quarry is more than 150 m. They display three major facies types according to dominant biota: (1) rudist limestones; (2) limestones with *Bacinella*, (3) limestones with corals. This sequence records the passage from restricted conditions (wackestone/packstone with levels or oncoids of cyanobacteria and/or Bacinella) to an open-marine environment (wackestone/packstone with dasycladales, rudists, and corals in situ), and then a return to restricted conditions. The depositional cycles are delimited by erosional surfaces, condensation, or by abrupt changes in the microfacies. The micropaleontological association identified in the quarry consists of foraminifers and calcareous algae. Among the foraminifers we mention: *Girariarella prismatica* Arnaud-Vanneau, *Glomospira urgoniana* Arnaud-Vanneau, *Mesorbitolina texana* (Roemer), *M. Subconcava* (Leymerie), *Pseudolituonella conica* Luperto Sinni and Masse, *Sabaudia minuta* (Hofker), *S. auruncensis* Chiocchini and Di Napoli Alliata, *Troglotella incrustans* Wernli and Fookes. The calcareous algae assemblage consists of *Cylindroporella ivanovici* (Sokač), *Griphoporella cretacea* (Dragastan), *Montiella elitzae* (Bakalova), *Neomeris cretacea* Steinmann, *Polystrata alba* (Pfender), *Parachaetetes asvapatii* (Pia), and newly found *Zittelina massei* n. sp. (Bucur et al., 2010).

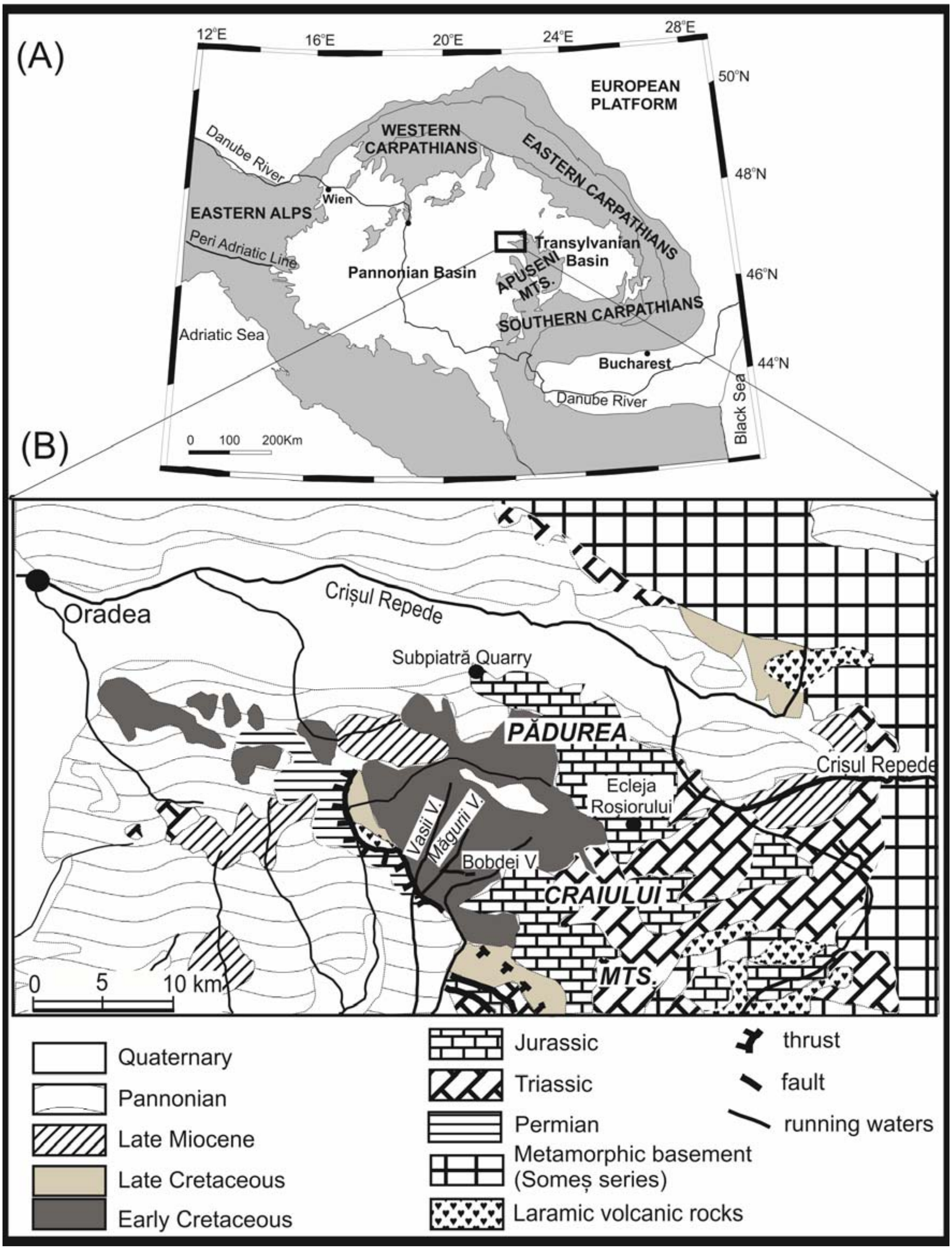

Figure 1. Location map (A) and simplified geological map of the Pădurea Craiului Mountains (B). The areas of sampling are shown using the geographical indications as in Table 1.

Table 1. Results of the $\delta^{18}O$ and $\delta^{13}C$ measurements on whole rock carbonate samples from Pădurea Craiului

Sample number	Age	Formation /Member	Location	Sample description	$\delta^{18}O$ vsSMOW	$\delta^{18}O$ vsPDB	$\delta^{13}C$ vsPDB
8725	Late Aptian-Albian	Vârciorog Fm.	Subpiatra Quarry (Recea Valley)	Limestone with Rudists	27.35	-3.41	4.23
8655				Limestone with Rudists	26.94	-3.85	4.19
8637				Limestone with Rudists	28.47	-2.37	3.75
8607				Limestone with Rudists	25.24	-5.49	3.92
8570				Limestone with Rudists	27.94	-2.88	4.67
8560				Limestone with Rudists	27.42	-3.39	4.69
4019				Limestone with Rudists	27.24	-3.56	2.97
4018				Limestone with Rudists	26.33	-4.44	2.65
537			Măgurii Valley	Shales/Marls	21.06	-9.55	0.74
614				Shales/Marls	21.02	-9.58	1.71
4297	Early Aptian	Valea Măgurii Fm.	Măgurii Valley	Limestone	25.18	-5.55	2.70
4289				Limestone	23.14	-7.53	3.39
4283				Limestone	25.93	-8.42	2.97
4280				Limestone	25.74	-5.01	3.24
4270				Limestone	26.00	-4.75	3.03
4263				Limestone	23.03	-7.63	2.79
4259				Limestone	23.58	-7.01	2.38
4256				Limestone	26.50	-4.26	2.69
4250		Ecleja Fm.	Măgurii Valley	Shales/Marls	21.74	-8.88	1.76
4165			Ecleja Rosiorului	Shales/Marls	27.00	-3.79	2.99
4164				Shales/Marls	25.92	-4.84	2.28
4163				Shales/Marls	24.11	-6.60	1.98
4353			Vasii Valley Ioanii Cornii stream	Shales/Marls	26.18	-4.59	0.82
4356				Shales/Marls	26.58	-4.20	0.46
4357				Shales/Marls	26.07	-4.69	2.38
4315		Ecleja Fm./ Valea Bobdei M.	Bobdei Valley	Limestone	26.88	-3.91	2.69
4316				Limestone	27.20	-3.58	2.62

4. ANALYTICAL TECHNIQUES

For carbon and oxygen isotope measurements, samples were crushed to 100 µm mesh size and heated at 400ºC for about 30 minutes in order to drive off volatile organic compounds. The CO_2 for mass spectrometer analysis was obtained from the reaction of carbonate with 100 % phosphoric acid, at 25ºC (McCrea, 1950). The gas was collected, purified and analyzed using a Delta V Advantage mass spectrometer at the Institute of Isotopic and Molecular Technology, Cluj-Napoca. The working standard was Carrara marble, with $\delta^{13}C$=+1.96‰ and $\delta^{18}O$=-1.96‰. Measured data were corrected using Craig's formula (Craig, 1957). The random analytical error is less than 0.07 ‰. Recorded δ values are the mean values of replicate runs. All isotope data are reported in conventional δ notation relative to the PDB standard.

Due to the presence in the analyzed samples of both calcite and dolomite in various ratios, some details on the analytical procedure are worthy of mention. The methods of investigation and calculation of the isotopic ratios are the same for both minerals, but the procedure of extraction of CO_2 is slightly different. The CO_2 released during the first hour of reaction has essentially the same δ values as that from pure calcite; as the reaction follows, CO_2 collected between 4 to 72 h has the same δ values as that from pure dolomite (Degens & Epstein, 1964). In our investigation, the acidic attack was performed for 1 h, in order to prevent the contribution of the carbon and oxygen isotopes from dolomite in the resulting CO_2. Thus, we considered that the isotopic compositions were indicative only for the syngenetic processes, which lead to the formation of calcite, and were probably not influenced by the diagenetic environment that transformed part of the calcite into dolomite.

5. RESULTS AND DISCUSSION

5.1. Carbon and oxygen isotope stratigraphy

The measured isotope ratios are presented in Table 1, and in figure 2 where they are plotted against various other data from literature. The measured $\delta^{18}O$ and $\delta^{13}C$ curves show clear patterns with major negative spikes and positive bulges. The Early Aptian to Late Albian O and C curves established in Pădurea Craiului can be correlated with other Early Cretaceous sections from the Alps (SE France, NE Italy, Swiss Prealps) (e. g. Menegatti et al., 1998, Herrle et al., 2004; Renard et al., 2005; Takashima et al., 2006; Kuhnt & Moullade, 2007), Outer Western Carpathains (e. g. Michanik et al., 2008), and mid-Pacific (e. g. Jenkyns, 1995). No data is available for the Apuseni Mountains. Here we compare them against the most complete Aptian/Albian dataset to date (Weissert & Erba, 2004; Kuhnt & Moullade, 2007; Keller, 2008; Föllmi et al., 2006).

5.1.1. The Early Aptian OAE1a event

The C-isotope curve shows, as its most striking feature, a significant negative excursion from a background of 2 to 3‰ to values as low as 0.46‰ in the Early Aptian. These low $\delta^{13}C$ values have been measured in a metric banc of black shales laying above the Valea Bobdei limestones. The C-isotope negative excursion is accompanied by a prominent decrease of the $\delta^{18}O$ values. Following the pronounced drop in the $\delta^{13}C$ values, there is an abrupt increase in values to form a peak, which is followed by a steep decrease.

There is no obvious co-variance between carbon and oxygen. However, there is a general tendency in the decreasing of the $\delta^{18}O$ values during Early Aptian indicating either a warming trend or a freshening from the surface waters or a combination of both.

The carbon and oxygen isotope negative excursion enable a comparison of the black shales of the upper Early Aptian Ecleja Formation with the well-known Selli Event (Menegatti et al., 1998). Subsequent increase of the $\delta^{13}C$ values corresponds to the OAE1a and implies anoxic depositional regime (depositional, productive, and stagnant). In such a regime, organic carbon is enriched in the lighter isotope ^{12}C and as a consequence of the increased burial rates of organic matter, an increase in the $^{13}C/^{12}C$ ratio in sea water is produced which is transmitted to skeletal and inorganic carbonate (Davey & Jenkyns, 1999 and literature therein). The amplitude of the C-isotopic sift during the OAE1a in Pădurea Craiului (from 0.45 to 2.99‰) is similar with the evolution of the $\delta^{13}C$ record recognized in Cismon, Italy (Menegatti et al., 1998).

5.1.2. The Fallot major $\delta^{13}C$ perturbation

For the interval corresponding to the Valea Măgurii Formation (Late Aptian), the carbon-isotope profile from Pădurea Craiului follows the same general trend as from the Tethyan-Atlantic region. The oxygen isotope curve is much more ‘noisy’ than the carbon one, oscillating from -4.26‰ to -8.42‰. Such large fluctuations were not yet reported for the same interval and could be a local characteristic.

In the lower part of the Vârciorog Formation (Late Aptian) the marlstone and black shale interval suggest an enhanced burial of organic matter due to more eutrophic conditions and resulting in low oxygen conditions at the seafloor. The decrease in the stable carbon isotope values (0.74 to 1.71‰) records a major climate-induced perturbation of the global carbon system and may have resulted in a reduced water mass exchange between the Pădurea Craiului Basin and the Tethyan Ocean. This succession can be correlated with the Late Aptian Niveau Fallot black shale succession from the Vocontian Basin (SE France) (Bréhéret, 1988).

5.1.3. The Late Aptian-Early Albian OAE1b event

The lower part of the Subpiatră limestones belonging to the Vârciorog Formation (Late Aptian – Albian) are characterized by lower $\delta^{13}C$ values (from 2.95 to 2.97‰) compared to the values recorded in its upper part (from 3.75 to 4.70‰). Such a considerable increase of the $\delta^{13}C$ values from 2.95‰ to 4.70‰, followed by a small drop down to 3.75‰, and then another increase up to 4.23‰ is characteristic of the OAE1b (Weissert & Erba, 2004 and literature therein). However, the amplitude of positive excursion is larger than other C-isotope positive excursions reported for northern Tethian region (Herle et al., 2004; Fölmi et al., 2006). Such high $\delta^{13}C$ values have been recorded in the Pacific realm (Price, 2003). During the latest Aptian and Early Albian the $\delta^{18}O$ values increase, suggesting cooling episodes and or an increase in salinity.

Within the Pădurea Craiului, the positive C-isotope spikes recorded in Late Aptian – Albian correspond to the level of limestones with *Bacinella* and include the level with *Zittelina massei* n. sp. (Bucur et al., 2010). It is important to note that the main feature of the newly described calcareous algae species is that it shows both an internal and external calcified wall. As this feature correlates with positive C-isotope excursion, as well as with significant temperature changes (see the oxygen isotope profile) it could indicate climat-induced perturbation of the global carbon system which provoked changes in biocalcification pattern. Herrle & Mutterlose (2003) also documented a cooling trend in the latest Aptian-early Albian in the Vocontian Basin based on increasing percentage of boreal nannofossil taxa. As isotopic and paleontological evidence of cooling correlates with the late phase of the C-isotope excursion it could mean that cooling episodes may have been a consequence of increased organic carbon burial and pumping of CO_2 from the atmosphere into sediments, as recorded in the positive shift of carbon isotope values (Weissert & Erba, 2004). Along with temperature changes, depositional cycles (Bucur et al., 2010) (i.e. the passage from restricted conditions to an open-marine environment, and then a return to restricted conditions) could have produced salinity changes, having a combined impact on the oxygen isotope profile.

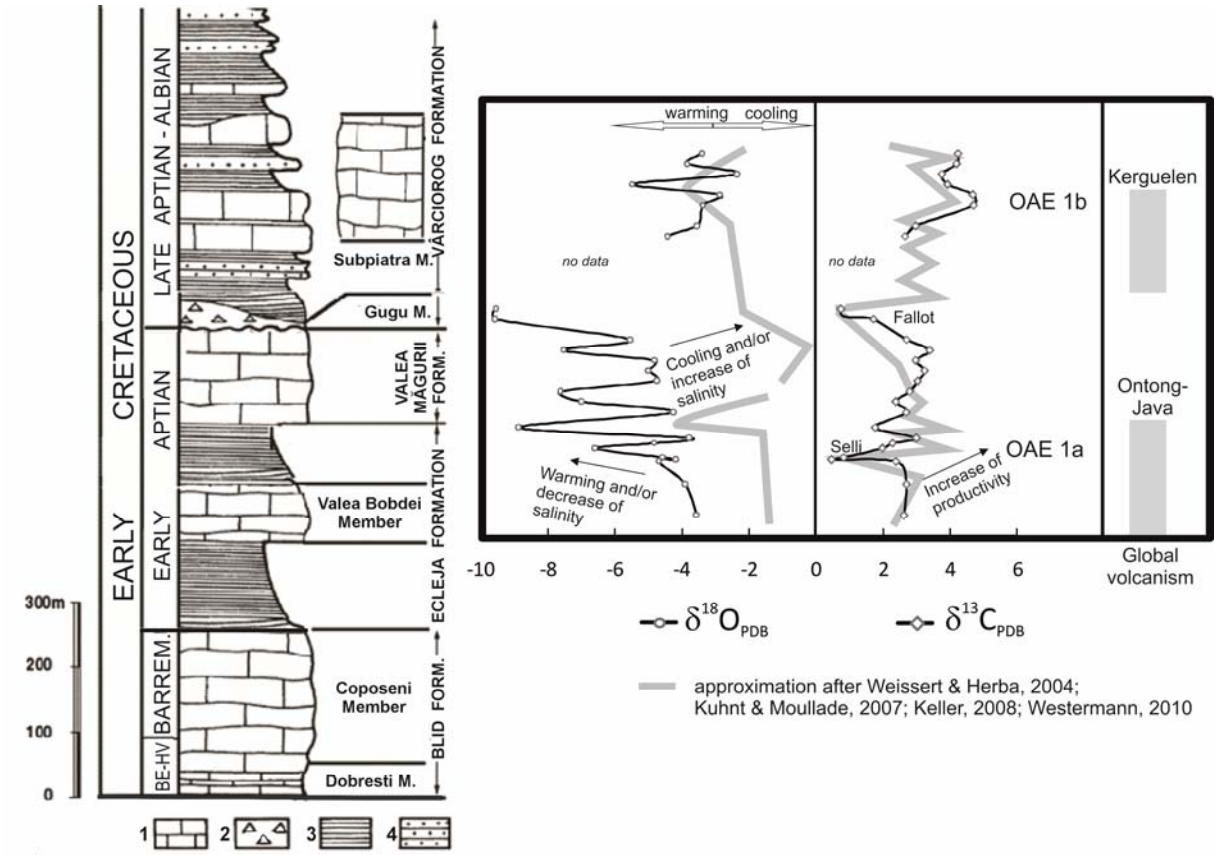

Figure 2. Early Aptian to Albian O- and C-isotope stratigraphy from Pădurea Craiului showing the principal features discussed in the text. Pre-existing isotope data from the Western Thetys are also shown (data from Weissert & Herba, 2004; Kuhnt & Moullade, 2007; Keller, 2008; Föllmi et al., 2006). Global volcanic phases after Keller, 2008. Lithology of the Early Cretaceous deposits in the Pădurea Craiului Mountains: 1 limestone; 2 breccia; 3 shales/marls; 4 sandstone.

5.2. Weathering pattern

Wortmann et al., (2004) propose a model for the altered carbon cycling and coupled changes in Early Cretaceous weathering patterns based on integrated carbon isotope and sandstone records of the western Tethys. After a pre-Aptian arid climate with little fluvial discharge favouring carbonate-dominated coasts for most of southern Europe, the Early Cretaceous (late Aptian to Albian) is characterized by the widespread disappearance of carbonate platforms, and the formation of continental deposits suggesting humid climate and intense weathering (e.g. bauxites, kaolinite glauconitic sandstones). The correlation between the unique occurrence of glauconite-bearing mature quartz sandstones and the Aptian carbon cycle perturbation suggests that these deposits may be related to increased weathering caused by elevated pCO_2 levels and accelerated hydrological cycling. The authors also propose two major transgressions during the Early and Late Aptian, interrupted by a lowstand in the Middle Aptian.

Similar to previously documented Thetyan regions, the sedimentological data recorded in the lower part of the Vârciorog Formation from Pădurea Craiului (i. e breakdown of carbonate platform and formation of the Gugu Breccia, intensified weathering and hydrological cycling as recorded by the presence of glauconite-bearing sandstones and bauxite deposits) that correlate with altered carbon cycling and low $\delta^{18}O$ values, also point out to long-term changes in weathering and erosion patterns and a transient climate regime during the Early Cretaceous to a green-house world (Late Cretaceous).

5.3. Oceanic anoxic events and large igneous province volcanism

Causality between large igneous provinces (LIPs) volcanism and OAEs implies that high concentrations of dissolved biolimiting metals (nitrogen, phosphorous, and silicon) enter into the oceans. In addition, CO_2 outgassing during volcanism may increase global temperature. The volume of crust produced by LIPs in the Cretaceous was almost three times greater than the prior and subsequent time periods (Keller, 2008). Two major intervals of LIPs eruption occurred during early Cretaceous: Late Barremian (with Ontong Java

Plateau and Manihiki Plateau construction in the Pacific), and Late Aptian to Early Albian (Kerguelen Plateau in the Indian Ocean).

Existing metal data from Cismon section (Italy) appear to record Ontong Java Plateau volcanism (122 Ma) in strata within and directly below the Selli Level, providing a possible causal scenario for OAE1a (e. g. Duncan & Huard, 1997). The major volcanic activity which generated the basalts from the Kerguelen Plateau, begun at about 118-119 Ma and possible continued at decreased rates till about 110 Ma and contributed to OAE1b (Jones & Jenkyns, 2001; Keller, 2008). While OAE1a is globally documented and related to Ontong Java Plateau volcanism, the OAE1b is of regional development.

In Pădurea Craiului, the Early Cretaceous deposits show stratigraphic evidence of anoxia (e. g. organic-rich facies, preserved laminae and/or distinctive biotic assemblage), as well as altered carbon cycling as our study revealed, spanning OAE1a and OAE1b, respectively. These findings suggest that both Ontong Java Plateau volcanism and Kerguelen Plateau volcanism might have influenced the paleoenvironmental setting. Further chemostratigraphic studies based on metal content of the Early Cretaceous deposits from Pădurea Craiului are necessary in order to document the relationship between LIPs, OAEs, and climate changes.

6. CONCLUSIONS

We have analysed 27 samples of whole rock carbonates for carbon and oxygen isotopes, thus generating the first baseline trends for $\delta^{13}C$ and $\delta^{18}O$ of Aptian to Early Albian deposits from the Pădurea Craiului Mountains. Our isotope data allowed us to recognize the presence of two major $\delta^{13}C$ positive excursions that have been attributed to the oceanic anoxic events 1a (within the upper part of Ecleja Formation and Valea Măgurii Formation) and 1b (within the Subpiatră Member of the Vârciorog Formation).

From a background of 2 – 3‰, a significant $\delta^{13}C$ negative excursion to values as low as 0.46‰ has been recorded in the Early Aptian preceding the OAE1a. Subsequent increase of the $\delta^{13}C$ values may be attributed to changes in bioproductivity. In an anoxic depositional regime, organic carbon is enriched in the lighter isotope ^{12}C and, as a consequence of the increased burial rates of organic matter, an increase in the $^{13}C/^{12}C$ ratio in sea water is produced and transmitted to skeletal and inorganic carbonate.

A second major $\delta^{13}C$ negative excursion was found in the shale deposits of the basal part of the Vârciorog Formation (Late Aptian) and has been correlated to the Late Aptian Niveau Fallot shale succession from the Vocontian Basin. The low $\delta^{13}C$ values within this stratigraphic interval correspond to low $\delta^{18}O$ values reflecting a combined impact of temperature increase and decline in seawater salinity, likely a reflexion of an influx of meteoric waters.

In the latest Aptian-Lower Albian, higher oxygen isotope values reflect a cooling trend. The cooling episodes may have been a consequence of increased organic carbon burial and sequestration of CO_2 from the atmosphere into sediments, as recorded in the positive shift of carbon isotope values. This event is assigned to OAE1b.

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