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Meteoric diagenesis of Upper Cretaceous and Paleocene–Eocene shallow-water carbonates in the Kruja Platform (Albania): geochemical evidence

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Abstract: In the central part of the Kruja Platform (Albania) located in the Apulian passive margin, geochemical analyses (calcimetry, Sr, REE and isotopic, $\delta^{13}C$ and $\delta^{18}O$) coupled with sedimentological and sequence stratigraphic study were carried out on Upper Cretaceous (CsB4, CsB5, CsB6 Biozones) and Paleocene to Middle Eocene shallow-water carbonates that crop out in the Kruje-Dajt massif (L'Escalier section) and Makareshi massif (La Route section). The lower values in Sr contents, the homogeneous $\delta^{18}O$ values in both sections and the covariance between $\delta^{13}C$ and $\delta^{18}O$ values (La Route section) are attributed to diagenesis influence by a meteoric water-buffer system, supported by petrographic observations. Moreover, a new exposure surface during the Late Cretaceous time (between CsB5 and CsB6 Biozones) may be proposed according to the low or negative excursions of Sr values, the negative excursions of isotopic values in both sections and a positive peak of normalized REE values (La Route section). These variations correlate with the geochemical signal reported by the decreasing strontium isotope values of rudist shells in the Island of Brač carbonate platform (Apulia domain) during the late Middle Campanian (77.3 Ma). Also, this continental exposure is consistent with the global sea-level fall reported from the Boreal Realm, North Atlantic, and the southern Tethyan margin. This geochemical evidence is a complementary tool for the sedimentological analysis and suggests a maximum regression (a sea-level fall) at the transition between the CsB5 and CsB6 Biozones. The high values of Sr content in Middle Eocene carbonates (L'Escalier section) reflect changes in depositional environment from restricted to open marine conditions. REE values increase through transgressive systems tract, characterized by small increase of detrital input. However, anomalies of certain values in both sections suggest disturbances linked either to the changes in clay input and to diagenetic modifications. Peaks in dolomite content are linked with regressive episodes or tendencies, and dolomitic facies, as indicated by intertidal-supratidal depositional environments.

Key words: Late Cretaceous, Paleocene, Middle Eocene, Albania, Kruja Platform, diagenesis, geochemistry, sedimentology, shallow-water carbonates.

Introduction

The evolution of Cretaceous carbonate platforms was influenced by global changes in the carbon cycle, climate and marine productivity (Schlanger & Jenkyns 1976; Weissert et al. 1998; Steuber 2002; Steuber & Veizer 2002).

Trace elements and carbon isotope stratigraphy realized in pelagic and hemipelagic carbonate successions combined with sedimentological analysis have been conducted to recognize systems tracts and sea-level changes for Cretaceous time (Jenkyns 1995; Bellanca et al. 1996; Perez-Infante et al. 1996; Weissert et al. 1998; Kump & Arthur 1999; Masse et al. 1999; Jarvis et al. 2001).

However, chemostratigraphy of shallow-water carbonate sediments remains understudied because the sedimentary record is often discontinuous and the geochemical data represents a combination of several signals, such as the depositional paleoenvironments, the paleosalinity and the influences of diagenesis, particularly important in these sediments (Vincent et al. 1997, 2004). The water-rock interaction of the diagenetic processes can modify the significance of the original chemical signal by the recrystallization of carbonate minerals. The oxygen isotope record in the Mesozoic and older carbonate rocks needs to be interpreted with cautions, because it is the product of the original record and an unknown input by meteoric water influx later, during post-depositional diagenetic alteration at elevated temperature, between 40° and 50° according to Sheu (1990) and Marshall (1992). Moreover, the carbon isotopic signal in Cretaceous carbonate platform is poor, often showing high-amplitude fluctuations because of the diagenetic overprint which complicates the identification of the time and nature of the events causing those variations (Joachimski 1994; Buonocunto et al. 2002). To overcome these problems, a multidisciplinary approach involving stratigraphic, sedimentological and geochemical data is recommended by several authors (Joachimski 1994; Vincent et al. 1997, 2004; Buonocunto et al. 2002).

This study presents geochemical data for the Upper Cretaceous and Paleocene to Middle Eocene carbonates of the Kruja Platform, a folded and overthrust zone which is recognized from South to North in Albania (Papa 1972; I.S.P.GJ. & I.GJ.N. 1983; Meço & Aliaj 2000; Robertson & Shallo

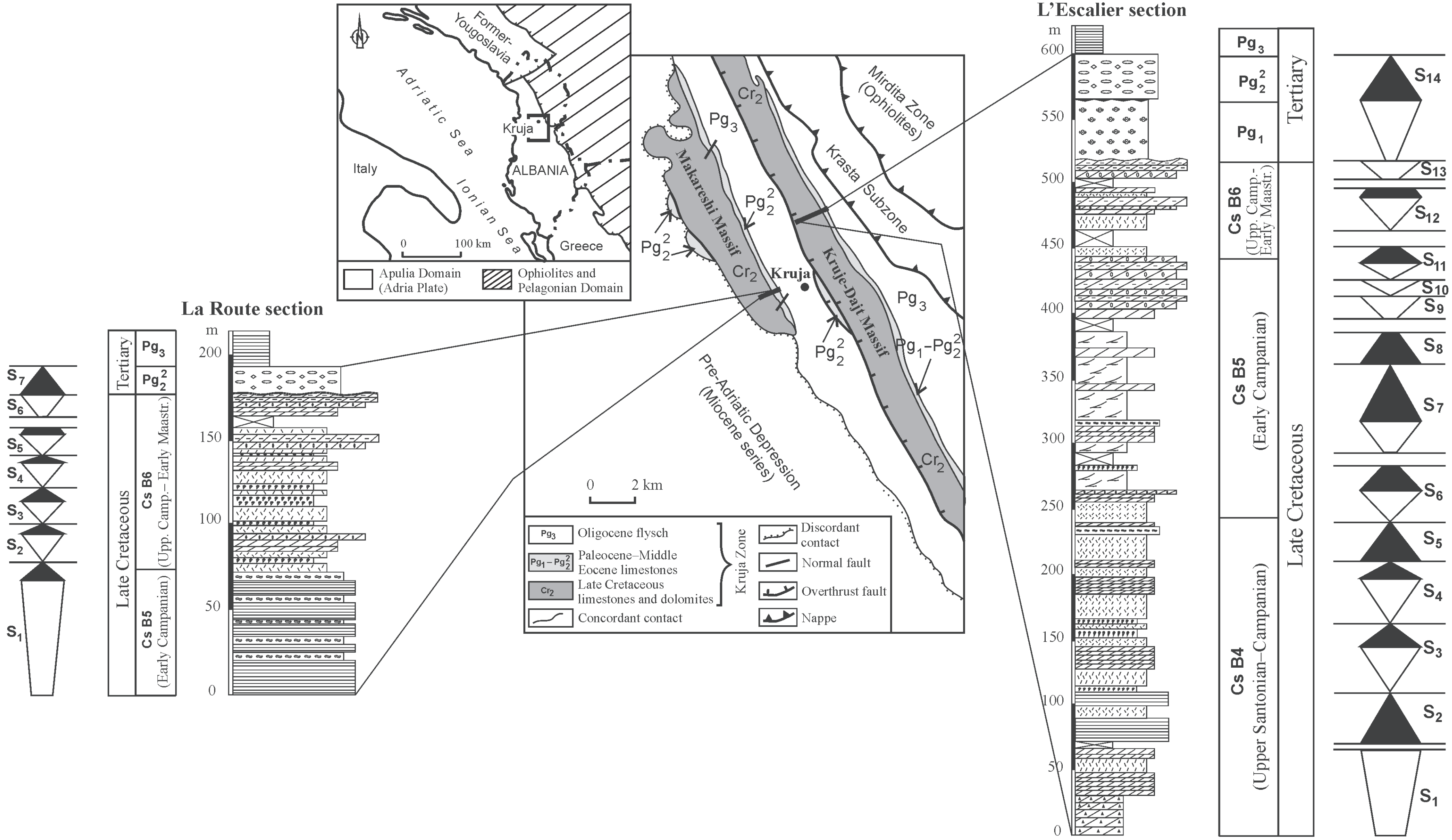

Fig. 1. Location, lithology and sequence stratigraphy of the studied sections (L'Escalier and La Route), and biostratigraphy of the Late Cretaceous to Eocene interval of the Kruja Platform (Albania). After I.S.P.GJ. & I.GJ.N. 1983; and Heba & Prichonnet (2006). Legend: Fig. 2.

2000): this platform is located in the Apulian passive margin which extended on both sides of the Adriatic and Ionian Sea (Fig. 1).

The two main objectives are: (1) to compare these results with the sedimentological and sequential results of this time interval where two periods of emersion are recognized, as described in Heba & Prichonnet (2006); and (2) to determine the relationship between the geochemical signal, depositional environments and diagenesis.

To achieve these goals, two sections of this platform have been analysed for carbonates, strontium and stable isotope ($\delta^{13}C$ and $\delta^{18}O$) content, and Rare Earth Elements (REE). The two sections presented there are the same as in the Heba & Prichonnet (2006): (a) the L'Escalier section in the Kruje-Dajt massif is composed of 360 m of limestones and 240 m of dolomitic rock; and (b) La Route section in the Makareshi massif includes 126 m of limestones and 49 m of dolomitic rock. Sample spacing was relatively large, representing only major facies and environmental changes, previously defined using sedimentological criteria, which should be coupled with geochemical signatures.

Geological setting

The studied sections cover the Late Santonian to the Early Maastrichtian stages of the Late Cretaceous, from 86 Ma to 70 Ma. Then both sections display a gap, the L'Escalier section extends into the Paleogene up to the Middle Eocene and the La Route section only to the Middle Eocene. Finally, Upper Eocene marls (in several locations) and Oligocene flysch cover the platform carbonates (starting at 39.4 Ma).

For the whole carbonate sequence, the biostratigraphic framework is mainly based on benthic foraminifers. The Late Cretaceous is divided into four biozones (Heba 1997; Heba & Prichonnet 2006) based on species of the Rhapydioninidae family (Fleury 1980), namely CsB4 (Late Santonian-Campanian), CsB5 (Early Campanian), CsB6 (Late Campanian–Early Maastrichtian) and CsB7 (Late Maastrichtian). With regard to the Tertiary, it is characterized by typical Paleocene and Middle Eocene miliolids and large hyaline foraminifers (Gjata et al. 1968; Peza 1973, 1977, 1982).

The stratigraphic succession is dominated by Upper Cretaceous neritic carbonates, limestones and dolomites, containing benthic foraminifers that were deposited in a confined subtidal to supratidal environment (Papa 1972; Peza 1973, 1975, 1977, 1982; I.S.P.GJ. & I.GJ.N. 1983; Heba 1997; Meço & Aliaj 2000; Robertson & Shallo 2000; Heba & Prichonnet 2006). Local variations of environments between the two sections are attributed to minor and common fluctuations of carbonate platforms, mainly due to facies succession; and in two periods of time, to eustatic variations which had caused two emergences (regressions) and temporal discontinuities at the end of the Cretaceous and Early Eocene times, also with some differences between the two sections. The major regression in the Kruja Platform began at the end of the Early Maastrichtian and extended for about 3 Myr in the L'Escalier section, where the CsB7 foraminiferal Biozone (Late Maastrichtian) is missing (Heba 1997; Heba & Prichonnet 2006), and about 20.5 Ma in the La Route section creating a gap ranging from Biozone CsB7 to the Early Eocene. Evidently these gaps include largely the Cretaceous/Tertiary boundary. The second regression is characterized by the presence of bauxite, but is only observed in the L'Escalier section: it lasted about 5 Myr during the Ear-

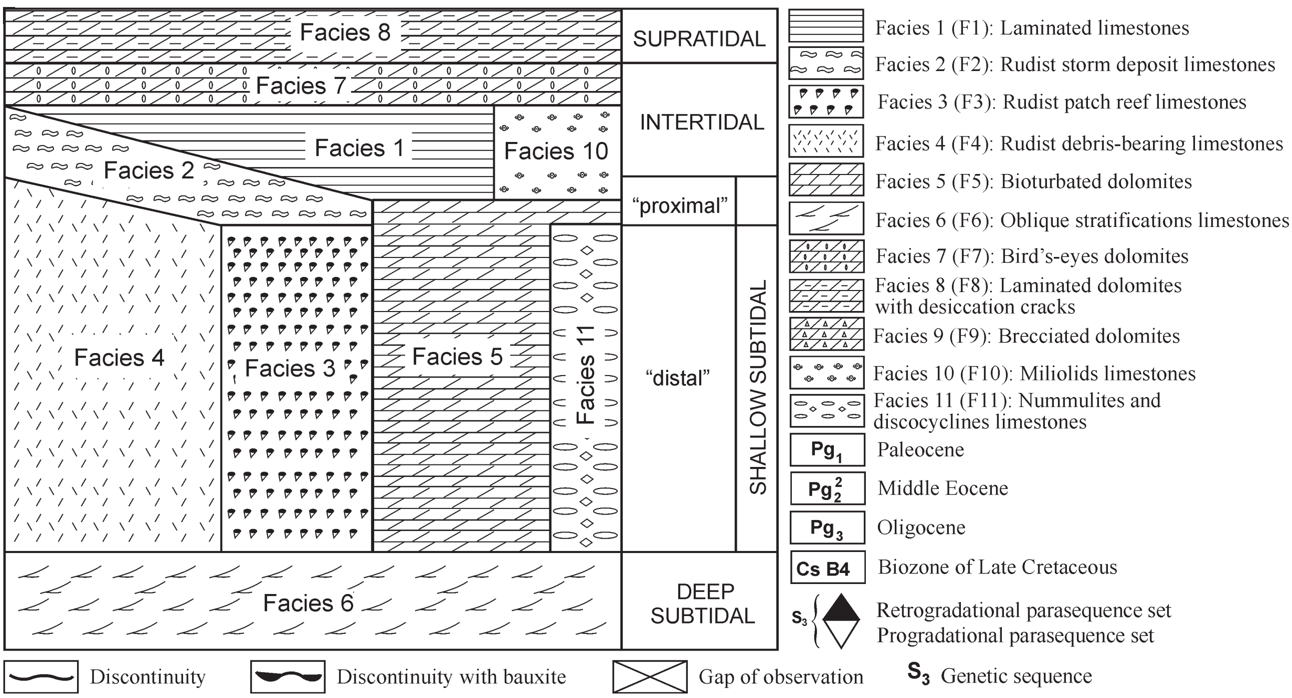

Fig. 2. Sedimentary depositional model of the facies succession (after Heba & Prichonnet 2006) and legend key.

ly Eocene. At the top of carbonate sequence in both sections, the Middle Eocene consists of organogenic limestones, deposited in an open shallow subtidal environment.

Sedimentological and sequence stratigraphical analysis

A general introduction to the facies analysis and sedimentary cycles of the L'Escalier and La Route sections is given here; further details may be found in Heba & Prichonnet (2006). The Upper Cretaceous to Paleogene carbonate deposits of L'Escalier and La Route sections display eleven sedimentary facies (F1 to F11; Fig. 2), ranging from subtidal to supratidal environments. These facies are arranged in a related sedimentary model as suggested by environmental interpretation of the depositional textures (Fig. 2). The deepest environments are characterized by limestones showing oblique stratifications (facies 6). Shallow subtidal environments are represented by: (1) rudist debris-bearing limestones (facies 4) which dominate both sections, (2) rudist patch reef limestones (facies 3), (3) dolomicrosparites displaying bioturbation traces (facies 5), and (4) bioclastic limestones (facies 11) containing large hyaline foraminifers (*Nummulites* and *Discocyclines*). Intertidal environments are represented by (1) laminated limestones attributed to microbial mats (facies 1), (2) rudist storm deposit limestones (facies 2), (3) bird's-eyes-bearing dolomites (facies 7), (4) miliolids-bearing limestones (facies 10), and (5) brecciated dolomites (facies 9) typical of intertidal channels. Supratidal environments are represented by laminated dolomites displaying desiccation cracks (facies 8). The dolomitic facies (facies 5, 7, 8 and 9) are interbedded with limestone facies in the Late Cretaceous part of the sedimentary succession and present idiotopic textures (euhedral, eorphyrotopic and eubhedral). These features demonstrate dolomitization during early diagenesis in a sebkha-type supratidal environment (Purser 1980; Walker & James 2000; Heba & Prichonnet 2006).

According to the depositional model of facies succession seven distinctive parasequences have been identified (Heba & Prichonnet 2006). Potential parasequence boundaries can be identified at this step based on one or more of the following stratigraphic criteria: sharp changes of facies, maximum flooding surfaces, transgression surfaces, clearly defined erosional truncation and direct evidence of subaerial exposure. From the recognition of progradational or retrogradational parasequence sets, fourteen genetic sequences (or cycles) *sensu* Cross (1988) can be determined in the L'Escalier section and seven in the La Route section (Fig. 1).

The maximum regression happened simultaneously in the two sections, at the thirteenth genetic sequence level (S13) in the L'Escalier section and at the sixth genetic sequence level (S6) in the La Route section (Fig. 1), characterized by an exposure surface at the end of CsB6 Biozone (Late Campanian–

Table 1: Calcimetry data for L'Escalier and La Route bulk sediment samples.

Sample	$CaCO_3$ %	$(CaMg)CO_3$ %	Facies	Sample	$CaCO_3$ %	$(CaMg)CO_3$ %	Facies
L'Escalier section (Kruje-Dajt massif)							
V2	23.88	78.56	F9	V198	24.95	72.93	F8
V3	20.87	81.94	F5	V203	26.22	71.64	F8
V12	15.88	86.95	F1	V208	98.62		F10
V31	21.19	81.62	F4	V208/1	93.13		F10
V32	28.73	72.58	F5	V209	97.18		F10
V36	97.64		F4	V209/1	91.28		F10
V45	89.96		F4	V204	98.77		F11
V54	83.56		F3	V205	83.22		F11
V48	92.50		F4	V206	94.61		F11
V51	81.21		F4	V207	79.58		F11
V57	97.15		F4				
V58	91.18		F4	La Route section (Makareshi massif)			
V62	87.13		F4				
V64	92.07		F4	M10	95.94		F1
V70	88.00		F4	M14	96.21		F1
V74	96.38		F5	M17	99.03		F1
V75	94.51		F5	M20	96.16		F1
V76	92.18		F4	M25	99.31		F1
V83	96.97		F4	M35	95.99		F1
V88	98.40		F4	M41	84.77		F1
V91	99.47		F2	M46	99.37		F1
V96	91.22		F4	M47	98.18		F2
V101	84.22	12.56	F6	M73	95.99		F2
V102	88.25		F6	M92	87.16		F2
V108	88.06		F3	M99	97.22		F1
V110	98.35		F6	M105	98.27		F2
V111	97.61		F6	M109	98.63		F1
V114	96.93		F4	M127	92.31		F2
V120	87.71	3.02	F2	M129	99.33		F4
V124	97.75		F6	M136	88.16		F4
V125	96.48		F6	M142	99.38		F3
V134	94.94		F6	M145	88.50		F4
V136	97.61		F6	Ms16	43.71	55.41	F5
V143	96.52		F4	M186	67.67	32.25	F7
V144	92.75		F6	M186/1	99.85		F4
V146	97.32		F6	M159	92.95		F4
V149	93.19		F4	M171	86.54	9.62	F3
V163	97.22		F4	M172	99.68		F4
V173	15.52	86.91	F7	M174	90.32	1.52	F4
Vs15	29.10	71.99	F8	M177	84.85	9.84	F4
V178	95.23		F4	M179	86.83	7.83	F3
V184	59.20		F4	M191	33.48	65.50	F5
V185	94.04		F4	M194	92.73	6.73	F4
V187	95.76		F4	M201	26.03	73.29	F5
V189	96.80		F4	M205	18.03	61.13	F7
V190	92.64		F4	M209	48.57	50.85	F8
V193	95.59		F4	M210	24.53	68.06	F8
V194	94.10		F4	M211	88.76	4.44	F11
V195	95.74		F4	M211/1	98.63		F11
V197	41.76	57.86	F7				

Notes: (a) Facies are indicated; (b) Stratigraphic positions of samples are indicated in Figs. 3 and 4.

Early Maastrichtian) (Heba & Prichonnet 2006). Similar episodes of regression associated with continental diagenesis or sedimentation (karstic fillings) are reported from the Maastrichtian time in other platforms of the Apulia domain (Gavrovo-Tripolitza in Greece — Mavrikas 1993 and Landrein et al. 2001; Island of Brač in Croatia — Gušić & Jelaska 1990). So, this regression recorded in these two sections of the Kruja Platform can be attributed with confidence to a global eustatic variation (relative sea-level fall) at the end of the Early Maastrichtian time.

Geochemical approach

Methods

A total of 96 bulk sediment samples (Table 1), 60 for the L'Escalier section and 36 for the La Route section, were selected for geochemical analysis. These provide a relatively good stratigraphic coverage of each main facies through the Late Cretaceous to Middle Eocene studied interval.

Calcimeter analysis of carbonates (limestone and dolomitic facies) was done on all the micrite samples in each section. The measurements were made with a Bernard-type apparatus at the Département des Sciences de la Terre et de l'atmosphère de l'Université du Québec à Montréal (UQAM).

Sr, stable isotopes and REE analyses were performed on samples containing 80 to 100 % calcite (33 samples for the L'Escalier section and 18 for the La Route section; Table 2). During sampling, as much as possible, the dolomitic facies were discarded. Moreover, visible fossils or shell fragments (*Nummulites*, *Discocyclines* and rudists) have not been included. Samples were crushed, and powered (5 g of powder) in an agate mortar to avoid contamination.

Carbon and oxygen isotopic measurements were done at the Stable Isotope Lab from GEOTOP-UQAM-McGill (Montréal, Québec) with a Micromass Isoprime™ spectrometer with Multicarb™ system. The isotopic results are reported against the VPDB (Vienna PeeDee Belemnite) international standard. Average precisions based on replicate analysis of selected samples or laboratory standards were ±0.1 ‰ for $\delta^{13}C$ and ±0.2 ‰ for $\delta^{18}O$.

Strontium (Table 2) and REE analyses (Table 3) were done at the OGS GeoLabs in Sudbury (Ontario) with an ICP-MS (IM-100) unit for samples prepared by the Open Beaker Digest method (code: OT4, brochure of OGS GeoLabs, 2003). Lower limits of detection for these trace elements are: 1 ppm for Sr, 0.05 ppm for La; 0.1 ppm for Ce; 0.04 ppm for Nd; 0.02 ppm for Sm; 0.01 ppm for Gd; 0.01 ppm for Dy; and 0.008 ppm for Er. Samples were digested in an open beaker using a combination of hydrofluoric, hydrochloric, nitric and/or perchloric acids. REE abundances were normalized (Table 4) to the average of North American Shale Composite values (NASC) given by Gromet et al. (1984): La = 31.1 ppm; Ce = 67.03 ppm; Nd = 30.4 ppm; Sm = 5.98 ppm; Gd = 5.5 ppm; Dy = 5.54 ppm; and Er = 3.27 ppm.

Table 2: Carbon and oxygen isotope, and strontium data for L'Escalier and La Route bulk sediment samples.

Sample	Sr (ppm)	$\delta^{13}C$ (‰ VPDB)	$\delta^{18}C$ (‰ VPDB)	Facies	Sample	Sr (ppm)	$\delta^{13}C$ (‰ VPDB)	$\delta^{18}C$ (‰ VPDB)	Facies
L'Escalier section (Kruje-Dajt massif)									
V36	303.92	1.67	–2.57	F4	V194	220.19	–0.98	–4.66	F4
V45	319.8	2.72	–2.16	F4	V195	530.7	2.68	–4.48	F4
V54	181.14	–1.63	–2.54	F3	V208	247.84	1.16	–2.42	F10
V48	328.74	2.12	–2.02	F4	V209	253.85	1.45	–2.43	F10
V51	284.61	1.65	–1.77	F4	V204	765.25	1.05	–5.78	F11
V64	262.81	3.12	–2.48	F4	V207	1016.68	1.01	–5.84	F11
V74	292.56	3.39	–3.42	F4					
V76	216.04	2.73	–2.79	F4	**La Route section (Makareshi massif)**				
V83	248.31	3.14	–2.44	F4					
V88	287.46	2.73	–4.05	F4	M10	351.32	0.90	–2.01	F1
V91	323.64	1.94	–3.95	F2	M46	305.71	–0.38	–2.43	F1
V96	346.63	2.50	–3.19	F4	M47	247.57	–4.05	–3.70	F2
V102	336.22	2.22	–3.94	F6	M92	199.19	–4.06	–3.70	F2
V108	285.78	2.91	–2.86	F3	M99	200.67	–4.13	–3.13	F1
V110	284.99	2.99	–3.43	F6	M105	345.59	–1.49	–3.09	F2
V114	414.6	2.09	–5.27	F4	M109	118.31	–4.30	–3.95	F1
V120	343.15	2.10	–4.17	F2	M127	361.81	–1.41	–3.47	F2
V125	271.15	1.83	–3.48	F6	M129	257.21	–0.51	–3.06	F4
V136	255.91	1.19	–3.69	F6	M136	258.76	1.72	–1.88	F4
V143	288.76	0.46	–4.67	F4	M145	234.51	0.66	–2.13	F4
V146	276.88	1.87	–2.33	F6	M159	281.09	0.66	–2.53	F4
V149	228.13	1.29	–3.39	F4	M171	312.73	1.46	–2.19	F3
V163	301.56	–2.08	–4.10	F4	M177	352.68	1.73	–2.44	F4
V178	188.3	–0.44	–4.93	F4	M179	257.66	1.10	–2.59	F3
V185	516.91	2.57	–2.64	F4	M194	389.64	1.96	–2.55	F4
V190	505.24	1.72	–4.10	F4	M211	318.09	–0.66	–3.80	F11
V193	461.88	1.44	–5.48	F4	M211/1	300.25	–0.56	–3.71	F11

Notes: (a) Facies are indicated; (b) Stratigraphic positions of samples are indicated in Figs. 3 and 4.

Table 3: Rare Earth Elements (REE) data for L'Escalier and La Route bulk sediment samples.

Sample	La (ppm)	Ce (ppm)	Nd (ppm)	Sm (ppm)	Gd (ppm)	Dy (ppm)	Er (ppm)	Facies
L'Escalier section (Kruje-Dajt massif)								
V36	0.22	0.16	0.08	0.02	0.01			F4
V45	0.34	0.65	0.31	0.07	0.09	0.09	0.06	F4
V54	0.27	0.21	0.17	0.03	0.02	0.02	0.01	F3
V48	0.12	0.15	0.06		0.01			F4
V51	0.15	0.20	0.13	0.03	0.01	0.02	0.01	F4
V64	0.49	0.22	0.18	0.04	0.04	0.04	0.02	F4
V74	0.45	0.11	0.12	0.03	0.02	0.02	0.02	F4
V76	0.19	0.11	0.09		0.02	0.02	0.01	F4
V83	0.26		0.09	0.02	0.01	0.01	0.01	F4
V88	0.39		0.08	0.02	0.02		0.01	F4
V91	0.34	0.15	0.22	0.06	0.04	0.04	0.03	F2
V96	0.31	0.15	0.15	0.02	0.03	0.02	0.01	F4
V102	0.2		0.07	0.02				F6
V108	0.27	0.37	0.18	0.04	0.02	0.03	0.02	F3
V110	0.44	0.10	0.06	0.02				F6
V114	0.24		0.06	0.02				F4
V120	0.09		0.07	0.02	0.01			F2
V125	0.2	0.21	0.11	0.02	0.03	0.02	0.02	F6
V136	0.27	0.19	0.14	0.03	0.03	0.03	0.02	F6
V143	0.12	0.11	0.10	0.02	0.01		0.00	F4
V146	0.55	1.10	0.60	0.12	0.10	0.09	0.05	F6
V149	0.2	0.18	0.14	0.04	0.03	0.03	0.02	F4
V163	0.18	0.19	0.10	0.03	0.02	0.01	0.01	F4
V178	0.25		0.06	0.00	0.00			F4
V185	0.22		0.09	0.02	0.00			F4
V190	0.14	0.26	0.14	0.04	0.02	0.02	0.01	F4
V193	0.18		0.08					F4
V194	0.58	0.85	0.54	0.11	0.12	0.12	0.07	F4
V195	0.41	0.24	0.18	0.04	0.02	0.02	0.01	F4
V208	0.38		0.12	0.03	0.02	0.02	0.02	F10
V209	0.28		0.11	0.03	0.02	0.02	0.02	F10
V204	1.28	1.28	0.93	0.2	0.24	0.23	0.15	F11
V207	1.64	1.81	1.25	0.26	0.31	0.29	0.19	F11
La Route section (Makareshi massif)								
M10	0.16	0.18	0.10	0.02	0.02	0.02	0.01	F1
M46	0.35	0.28	0.22	0.05	0.06	0.05	0.04	F1
M47	0.28	0.34	0.17	0.03	0.04	0.03	0.02	F2
M92	0.39	0.14	0.11	0.03	0.02	0.02	0.01	F2
M99	0.19	0.36	0.17	0.03	0.04	0.04	0.03	F1
M105	0.41	0.19	0.10	0.02	0.02	0.02	0.01	F2
M109	0.58	1.02	0.54	0.11	0.14	0.12	0.07	F1
M127	0.38	0.78	0.41	0.1	0.1	0.08	0.04	F2
M129	0.49	0.80	0.51	0.1	0.1	0.07	0.03	F4
M136	0.06		0.06					F4
M145	0.35							F4
M159	0.18		0.08		0.01			F4
M171	0.27	0.24	0.17	0.04	0.04	0.03	0.02	F3
M177	0.25	0.14	0.08		0.02	0.02	0.02	F4
M179	0.06		0.05					F3
M194	0.37	0.38	0.22	0.04	0.04	0.04	0.02	F4
M211	0.73	0.63	0.44	0.1	0.12	0.11	0.08	F11
M211/1	0.72	0.60	0.45	0.08	0.1	0.1	0.07	F11

Notes: (a) Facies are indicated; (b) Stratigraphic positions of samples are indicated in Figs. 3 and 4.

Description of geochemical variations

Calcimeter measurements

Calcite is the dominant carbonate mineral in the analysed micrites of both sections (Table 1, Figs. 3 and 4).

In the L'Escalier section (Table 1), where 60 % of the carbonates are limestones, the calcite content is generally between 75 % and 95 % (for 80 % of analysis). However, peaks of dolomite ranging from 71.6 to 87 % are identified in this series of limestones in some samples (Fig. 3): V2, V3, V12, V31, V32 and V203.

In the La Route section (Table 1), with 75 % limestones, calcite represents between 85 % and 95 % of the carbonate content (for 80 % of analyses). Dolomite peaks ranging from 55.4 to 73.3 % are restricted to the CsB6 Biozone, and to the samples Ms16, M191, M201 and M210 (Fig. 4).

Strontium measurements

Three main features of the Sr contents are observed in the L'Escalier section (Fig. 5): (1) the fluctuation of lower values, ranging from 200 to 400 ppm (samples V36 to V178, Table 2), in Cretaceous limestones corresponding to the

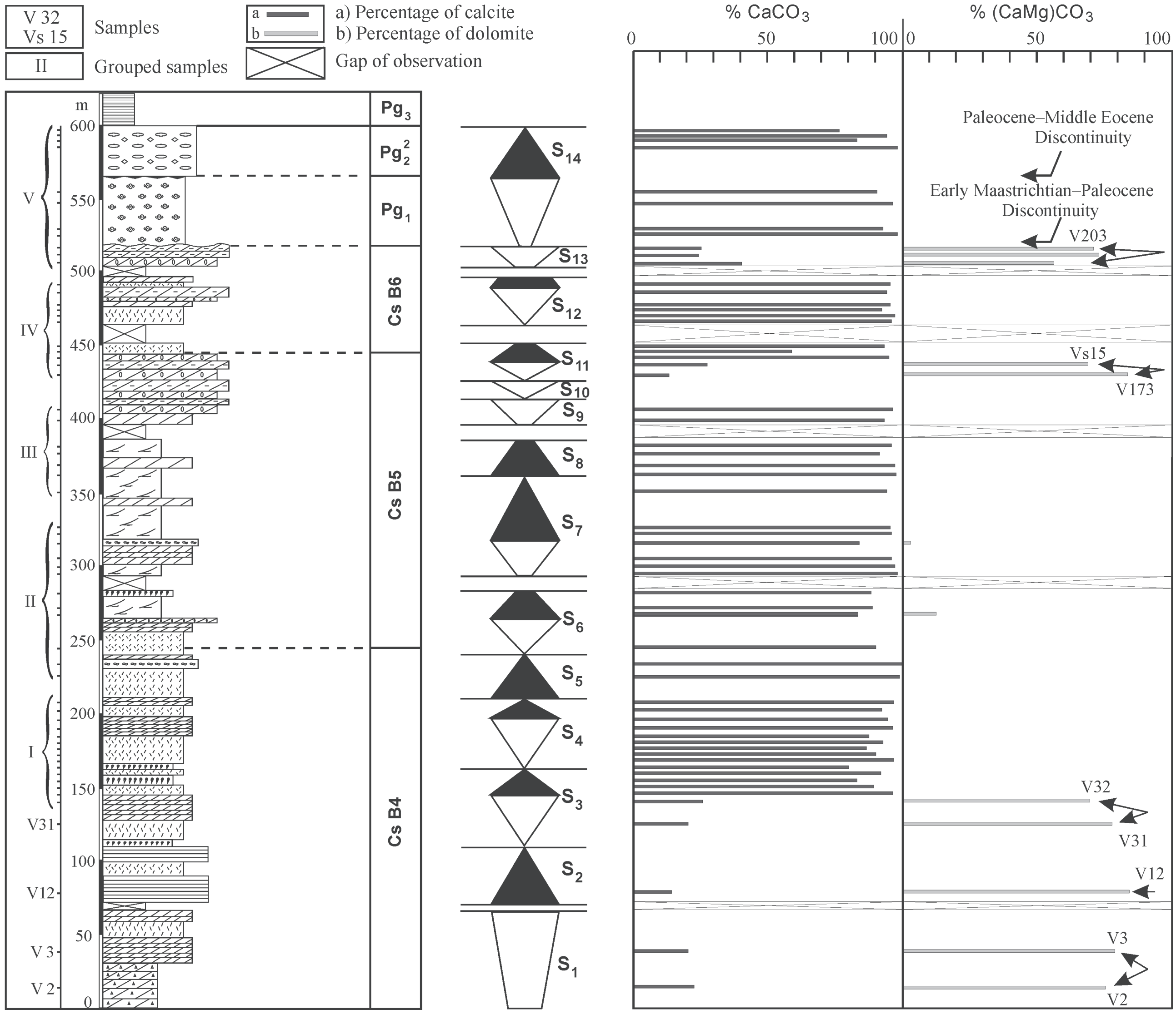

Fig. 3. Calcimetry profile for the L'Escalier section (Kruje-Dajt massif). Data are listed in Table 1. Legend: Fig. 2. Note: Stratigraphic position of grouped samples: **I** — (V32, V36, V45, V54, V48, V51,V57, V58, V62, V64, V70, V74 to V76, V83); **II** — (V88, V91, V96, V101, V102,V108, V110, V111, V114, V120, V124, V125); **III** — (V134, V136, V143, V144, V146, V149, V163); **IV** — (V173, Vs15, V178, V184, V185, V187, V189, V190, V193 to V195); **V** — (V197, V198, V203, V208, V208/1, V209, V209/1, V204 to V207).

CsB4 and CsB5 Biozones; (2) the increase of the Sr contents to about 500 ppm in Biozone CsB6, although there are some lower values of about 250 ppm in two samples of facies 10 (V208 and V209; Paleocene miliolids limestones); and (3), the highest values found in nummulites and discocyclines Middle Eocene limestones (780 ppm in sample V204 and 1016 ppm in sample V207; facies 11).

In the La Route section (Fig. 6), the Sr curve displays: (1) mostly values ranging again from 200 to 400 ppm; and (2) a low value recorded near the top of the CsB5 Biozone (118 ppm, sample M109). However, in this section strontium values for the Middle Eocene limestones (facies 11) are much lower than those obtained for the same facies in the L'Escalier section (e.g. 318 and 300 ppm respectively in samples M211 and M211/1).

Stable isotope data

In the L'Escalier section (Fig. 5), carbon isotope values vary from −2.08 ‰ to +3.39 ‰. Most of the Upper Cretaceous limestones display positive $\delta^{13}C$ values, but three negative peaks were recorded in the upper part of Biozone CsB5 (samples V163, V178) and in Biozone CsB6 (sample V194). Thus, over most of Biozones CsB4 and CsB5, $\delta^{13}C$ values remain around 2 ‰. After a long-term decrease until the top of the CsB6 Biozone (sample V178), a rapid change back to positive values is observed (+2.57 ‰ in sample V185). Finally, after a $\delta^{13}C$ negative excursion (−0.98 ‰ in sample V194) there is a new positive shift (+2.5 ‰ in sample V195). The Tertiary limestones are characterized by $\delta^{13}C$ values near +1.1 ‰.

Table 4: Normalized REE data for L'Escalier and La Route bulk sediment samples.

Sample	La	Ce	Nd	Sm	Gd	Dy	Er	Facies
L'Escalier section (Kruje-Dajt massif)								
V36	0.007	0.002	0.003	0.003	0.002			F4
V45	0.011	0.010	0.010	0.012	0.016	0.016	0.018	F4
V54	0.009	0.003	0.006	0.005	0.004	0.004	0.003	F3
V48	0.004	0.002	0.002		0.002			F4
V51	0.005	0.003	0.004	0.005	0.002	0.004	0.003	F4
V64	0.016	0.003	0.006	0.007	0.007	0.007	0.006	F4
V74	0.014	0.002	0.004	0.005	0.004	0.004	0.006	F4
V76	0.006	0.002	0.003		0.004	0.004	0.003	F4
V83	0.008		0.003	0.003	0.002	0.002	0.003	F4
V88	0.013		0.003	0.003	0.004		0.003	F4
V91	0.011	0.002	0.007	0.010	0.007	0.007	0.009	F2
V96	0.010	0.002	0.005	0.003	0.005	0.004	0.003	F4
V102	0.006		0.002	0.003				F6
V108	0.009	0.006	0.006	0.007	0.004	0.005	0.006	F3
V110	0.014	0.001	0.002	0.003				F6
V114	0.008		0.002	0.003				F4
V120	0.003		0.002	0.003	0.002			F2
V125	0.006	0.003	0.004	0.003	0.005	0.004	0.006	F6
V136	0.009	0.003	0.005	0.005	0.005	0.005	0.006	F6
V143	0.004	0.002	0.003	0.003	0.002			F4
V146	0.018	0.016	0.020	0.020	0.018	0.016	0.015	F6
V149	0.006	0.003	0.005	0.007	0.005	0.005	0.006	F4
V163	0.006	0.003	0.003	0.005	0.004	0.002	0.003	F4
V178	0.008		0.002					F4
V185	0.007		0.003	0.003				F4
V190	0.005	0.004	0.005	0.007	0.004	0.004	0.003	F4
V193	0.006		0.003					F4
V194	0.019	0.013	0.018	0.018	0.022	0.022	0.021	F4
V195	0.013	0.004	0.006	0.007	0.004	0.004	0.003	F4
V208	0.012		0.004	0.005	0.004	0.004	0.006	F10
V209	0.009		0.004	0.005	0.004	0.004	0.006	F10
V204	0.041	0.019	0.031	0.033	0.044	0.042	0.046	F11
V207	0.053	0.027	0.041	0.043	0.056	0.052	0.058	F11
La Route section (Makareshi massif)								
M10	0.005	0.003	0.003	0.003	0.004	0.004	0.003	F1
M46	0.011	0.004	0.007	0.008	0.011	0.009	0.012	F1
M47	0.009	0.005	0.006	0.005	0.007	0.005	0.006	F2
M92	0.013	0.002	0.004	0.005	0.004	0.004	0.003	F2
M99	0.006	0.005	0.006	0.005	0.007	0.007	0.009	F1
M105	0.013	0.003	0.003	0.003	0.004	0.004	0.003	F2
M109	0.019	0.015	0.018	0.018	0.025	0.022	0.021	F1
M127	0.012	0.012	0.013	0.017	0.018	0.014	0.012	F2
M129	0.016	0.012	0.017	0.017	0.018	0.013	0.009	F4
M136	0.002		0.002					F4
M145	0.011							F4
M159	0.006		0.003		0.002			F4
M171	0.009	0.004	0.006	0.007	0.007	0.005	0.006	F3
M177	0.008	0.002	0.003		0.004	0.004	0.006	F4
M179	0.002		0.002					F3
M194	0.012	0.006	0.007	0.007	0.007	0.007	0.006	F4
M211	0.023	0.009	0.014	0.017	0.022	0.020	0.024	F11
M211/1	0.023	0.009	0.015	0.013	0.018	0.018	0.021	F11

Notes: (a) Facies are indicated; (b) Stratigraphic positions of samples are indicated in Figs. 3 and 4.

The $\delta^{18}O$ curve of the L'Escalier section (Fig. 5) displays values ranging from −5.84 to −1.77 ‰. In particular, a general decrease is observed from the base of the section to the end of the CsB5 Biozone (at the level of V178 sample), followed by a sharp positive shift. The Tertiary oxygen isotope curve shows a negative excursion with the lowest value (−5.84 ‰ in sample V207) at the top of the section. Some samples (V114, V193, V204 and V207) have $\delta^{18}O$ values smaller than −5 ‰, the limit for marine carbonate deposits in modern sediments according to James & Choquette (1990).

In the La Route section (Fig. 6), $\delta^{13}C$ values range from −4.30 ‰ to +1.96 ‰. At the base of the section, most $\delta^{13}C$ values are negative with a peak of −4 ‰ (sample M109) near the top of Biozone CsB5. A positive excursion follows, shifting to values of circa +1 ‰ (samples M127, M129 and M136). Above this positive excursion, $\delta^{13}C$ values mainly fluctuate between 0.6 ‰ and 1.96 ‰. At the top of the section, the limestones of the Middle Eocene display slightly negative $\delta^{13}C$ values (facies 11; −0.66 ‰ and −0.56 ‰ respectively in samples M211 and M211/1).

The $\delta^{18}O$ curve for this section shows very similar variations to the $\delta^{13}C$ curve. Two main features of the $\delta^{18}O$ record are observed in the Late Cretaceous: (1) the negative excursion with the lowest value (−3.95 ‰) in sample M109; and (2)

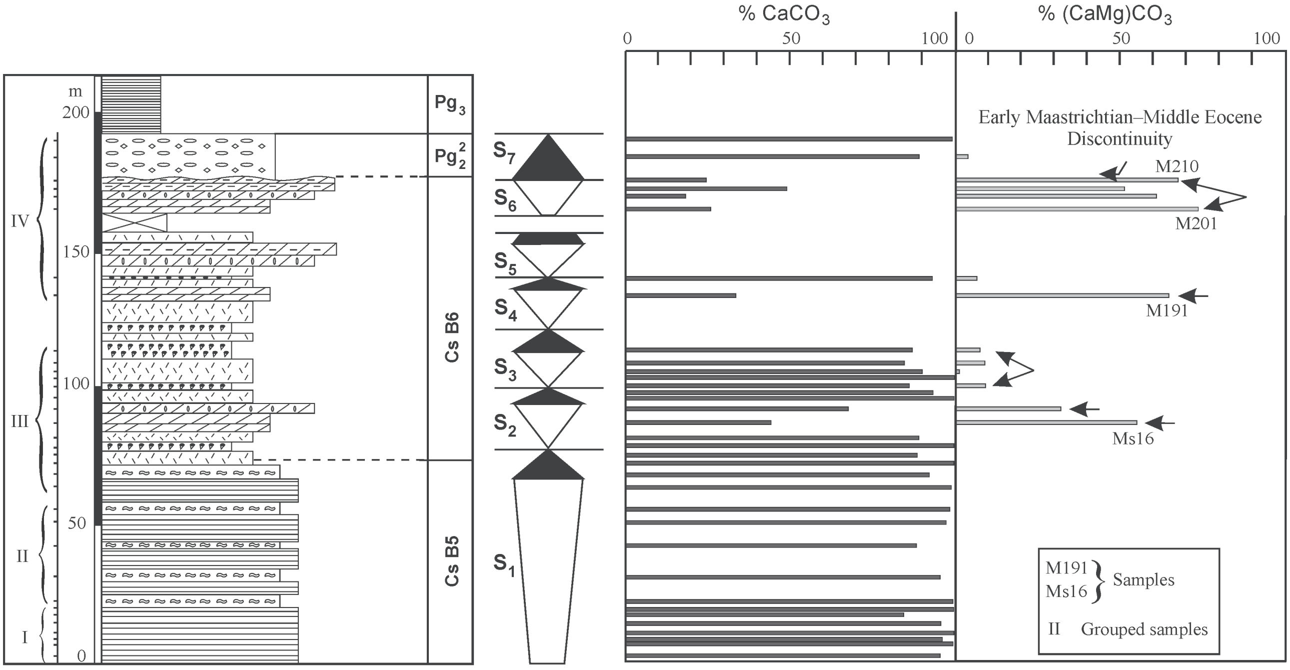

Fig. 4. Calcimetry profile for the La Route section (Makareshi massif). Data are listed in Table 1. Legend: Fig. 2. Note: Stratigraphic position of grouped samples: **I** — (M10, M17, M20, M25, M35, M41, M46); **II** — (M47, M73, M92, M99, M105); **III** — (M109, M127, M129, M136, M142, M145, Ms16, M186, M186/1, M159, M171, M172, M174, M177, M179); **IV** — (M191, M194, M201, M205, M209, M210, M211, M211/1).

the broad positive excursion followed by values mostly fluctuating around −2.4 ‰. In contrast to the L'Escalier section, the Middle Eocene limestones (facies 11) display here more negative values (−3.8 ‰ and −3.71 ‰ respectively in samples M211 and M211/1), similar to the negative peak identified by the sample M109.

Rare earth element (REE) measurements

In the L'Escalier section (Fig. 7), normalized REE values of the Late Cretaceous and the Paleocene limestones fluctuate between 0 and 0.025, whereas the highest values are recorded in the Middle Eocene limestones ranging from 0.019 to 0.058: normalized REE positive peaks (marked by black arrows) are distinguished in samples V45, V60,V91, V146, V194 and V207.

Normalized REE variations in the La Route section (Fig. 8) are less pronounced than in the other section. But during the Late Cretaceous time, a significant positive peak (sample 109) was recorded near the top of the CsB5 Biozone.

Interpretation of geochemical variations and discussion

Diagenetic effects on the trace elements and the isotopic signature

The strontium profiles for the Cretaceous carbonates of the L'Escalier section, corresponding to the CsB4 and CsB5 Biozones (samples V36 to V178; Fig. 5, Table 2) and for the entire La Route section (Fig. 6, Table 2), display depleted values between 200 and 400 ppm. They are very low in comparison with global values of Cretaceous pelagic limestones (500–900 ppm; Steuber 2002) and of Carboniferous micrites (700 to 3400 ppm; Wiggins 1986), which are interpreted and considered as initial marine values of carbonate sediment (Wiggins 1986; Steuber & Veizer 2002). Similar depleted values (ranging from 200 to 400 ppm) have been reported in the Bajocian-Bathonian and Middle Oxfordian carbonate-shelf sedimentary successions of the Paris Basin (France), (Vincent et al. 1997, 2006). According to Vincent et al. (2006) low strontium contents can be explained by the meteoric water-rock interactions involving freshwater fluids with very low Sr and Mg contents during burial diagenesis.

Bulk carbonates from the various depositional environments of the two sections show no significant differences in the oxygen isotope ratios (Figs. 5 and 6, Table 2). These values are relatively homogeneous, around −2.90 ‰ in the La Route section and −3.56 ‰ in the L'Escalier section. All these data might be interpreted as a result of diagenetic stabilization of the carbonate mud in an "open water-buffered oxygen system" (Joachimski 1994). During early diagenesis meteoric waters migrate through pore spaces, thus allowing chemical interactions between the water and rock constituents. In this way, the isotopically lighter meteoric water can overprint the carbonates, leaving a more depleted signature than the primary signature of deposition.

Petrographic observations have shown some valuable indications proving several phases of diagenesis: (a) early diagenesis as proved by the presence of crystals of dolomite scattered

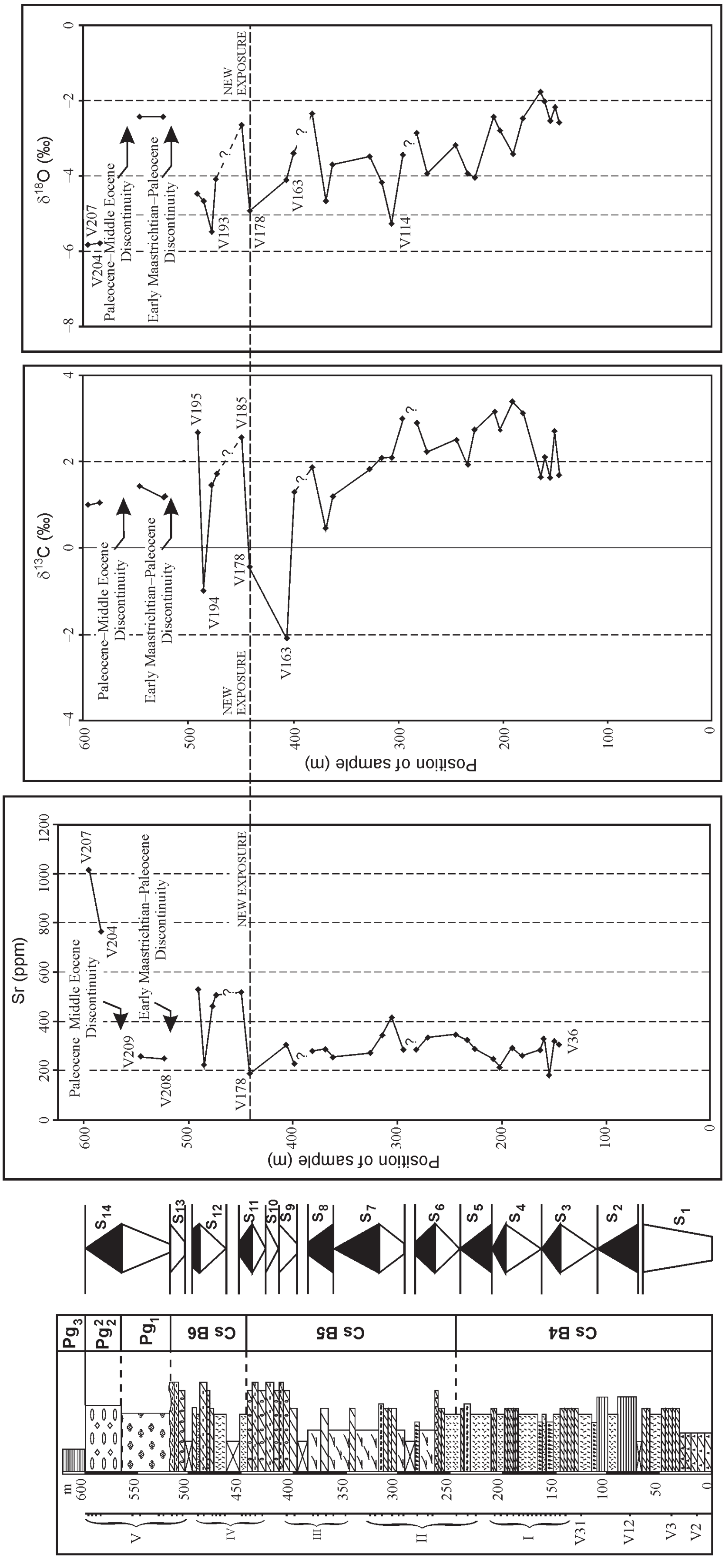

Fig. 5. Strontium and stable isotope profiles for the L'Escalier section (Kruje-Dajt massif). Data are listed in Table 2. Legend: Fig. 2.

in calcite matrix, partially recrystallized; (b) early to later diagenesis as proved by a coarse cement filling the residual porosity; and (c) late (burial ?) diagenesis as demonstrated by three stages of recrystallization in calcite veins (centripetal zonation: black, yellow and yellow-orange), as shown by cathodoluminescence analysis (thin section V163, L'Escalier section, Table 2) (Heba 1997).

In both studied sections (Figs. 5 and 6, Table 2), $\delta^{13}C$ and $\delta^{18}O$ appear to change in parallel. In carbonate platforms, positive covariance between $\delta^{13}C$ and $\delta^{18}O$ has been interpreted as a result of early diagenetic alteration of limestones in the marine-meteoric mixing zone (Joachimski 1994; Buonocunto et al. 2002; Allan & Matthews 2006). In the Kruja Platform, cross-plots of $\delta^{18}O$ vs. $\delta^{13}C$ values (Fig. 9) show a covariant isotopic trend for the La Route section (Fig. 9B) that is indicative of a clear diagenetic alteration, and a minor covariation for the L'Escalier section (Fig. 9A), suggesting a weaker diagenetic alteration.

In particular, isotope values decrease towards levels defined respectively by sample V178 in the L'Escalier section ($\delta^{13}C = -0.44$ ‰ and $\delta^{18}O = -4.93$ ‰) and sample M109 in the La Route section ($\delta^{13}C = -4.30$ ‰, $\delta^{18}O = -3.95$ ‰). These negative peaks are followed in the two sections by sharp positive shifts in $\delta^{13}C$ and $\delta^{18}O$ values. Moreover, the negative $\delta^{13}C$ and $\delta^{18}O$ values at the level of sample V178 in the L'Escalier section correspond to the end of the low Sr values (e.g. 200 to 400 ppm, Fig. 5), whereas in the La Route section, the negative isotopic peaks at the level of sample M109 correspond to the low value of Sr (e.g. 118 ppm, Fig. 6) and the positive peak in the normalized REE profile (Fig. 8). All these data seem to indicate subaerial exposure near the level of sample V178 in the L'Escalier section and near the level of sample M109 in the La Route section.

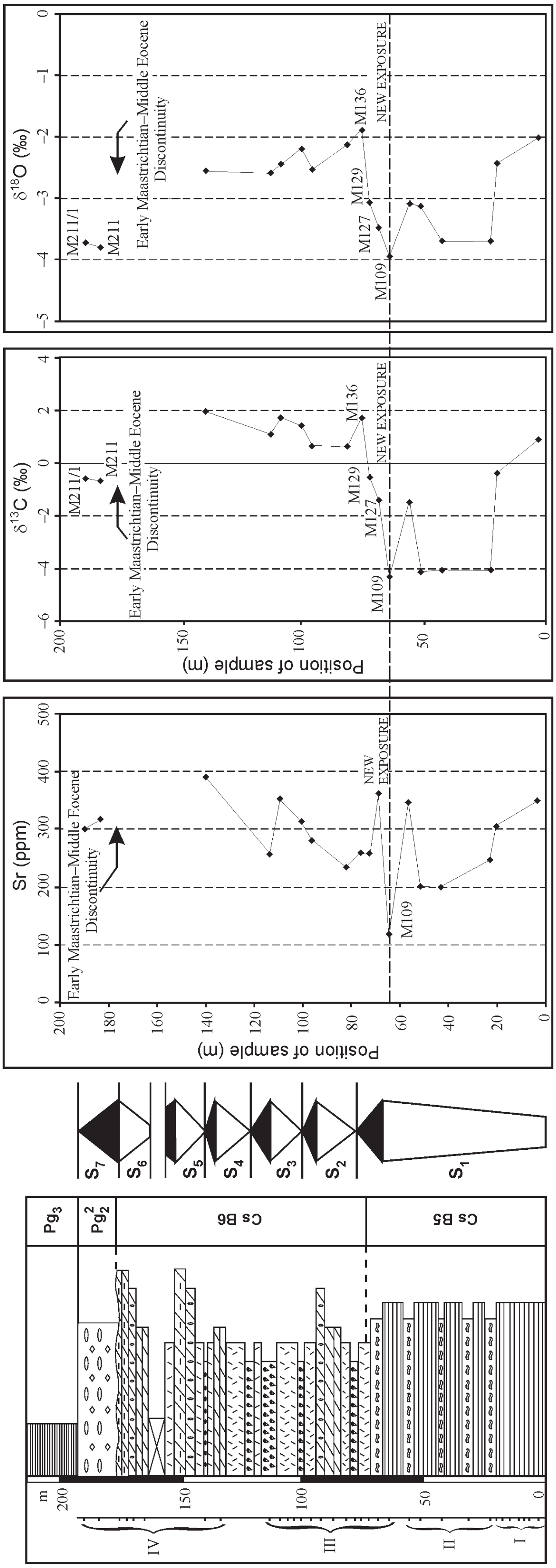

Fig. 6. Strontium and stable isotope profiles for the La Route section (Makareshi massif). Data are listed in Table 2. Legend: Fig. 2.

According to Joachimski (1994) and Buonocunto et al. (2002) the record of this kind of subaerial exposure, in both sections here, is related to soil-derived influence in $\delta^{13}C$ values and to meteoric diagenesis effect in $\delta^{18}O$ and Sr values. The positive peak in the normalized REE profile of the La Route section (sample M109, Fig. 8) may result from a probable weak pedogenetic influence near the exposed surface in this section and to an increase of detrital input during the transgressive phase of the S1 cycle (genetic sequence).

Geochemical patterns as indicators of system tracts and depositional environments

In the L'Escalier section, the exposure event at the level of sample V178 indicated by the end of the low values of Sr content and the decreasing trend of isotopic signatures (Fig. 5), corresponds to the transgressive surface of the progradational parasequence set of the S11 cycle (Heba & Prichonnet 2006). This semi-regression cycle characterized by the upper intertidal to supratidal environments (facies 7 and 8, Fig. 2) was followed by a sharp deepening of the environment (facies 4) that coincides with sharply rising Sr, $\delta^{13}C$ and $\delta^{18}O$ values. The subaerial event recorded in the La Route section (at the level of sample M109) by the low Sr content and the low $\delta^{13}C$ and $\delta^{18}O$ values (Fig. 6), and the positive peak on the normalized REE (Fig. 8) is consistent with the sedimentological interpretation (Heba & Prichonnet 2006): this event registered near a transgressive surface coincides with the inflection point between the progradational parasequence set of the S1 cycle (intertidal environment, facies 1 and 2, Fig. 2) and the facies 5 wich indicates a relatively deeper environment (subtidal).

In the two sections, these subaerial events are registered at the same stratigraphic position, between Biozones CsB5 (Early Campanian) and CsB6 (Late Campanian–Early Maastrichtian), at the regressive system tract (S11 in the L'Escalier and S1 in the La Route). That suggests a local maximum of the regression in the Kruja Platform. A similar episode of exposure is recognized at the same time during the late Middle Campanian (77.3 Ma) in the Island of Brač carbonate platform (Apulia domain, in Croatia) by decreasing strontium isotope values of low-Mg calcite of rudist shells (Steuber et al. 2005). This correlation reflects a larger inter-regional feature: all these platforms of the Apulia domain emerged at the same time. Moreover, this phenomenon is correlated with the global sea-level fall reported from the Boreal Realm, North Atlantic, and the southern Tethyan margin (Jarvis et al. 2002; Steuber et al. 2005). This evidence strongly suggests that the CsB5 sedimentation in the two sections was eustatically controlled and another maximum regression may have occurred at the transition between the CsB5 and CsB6 Biozones, a biostratigraphic limit (named the New Exposure in Figs. 5, 6 and 8).

The variations in Sr contents are known to reflect the paleosalinity of the seawater in which carbonates precipitate with increasing Sr contents reflecting increasing sa-

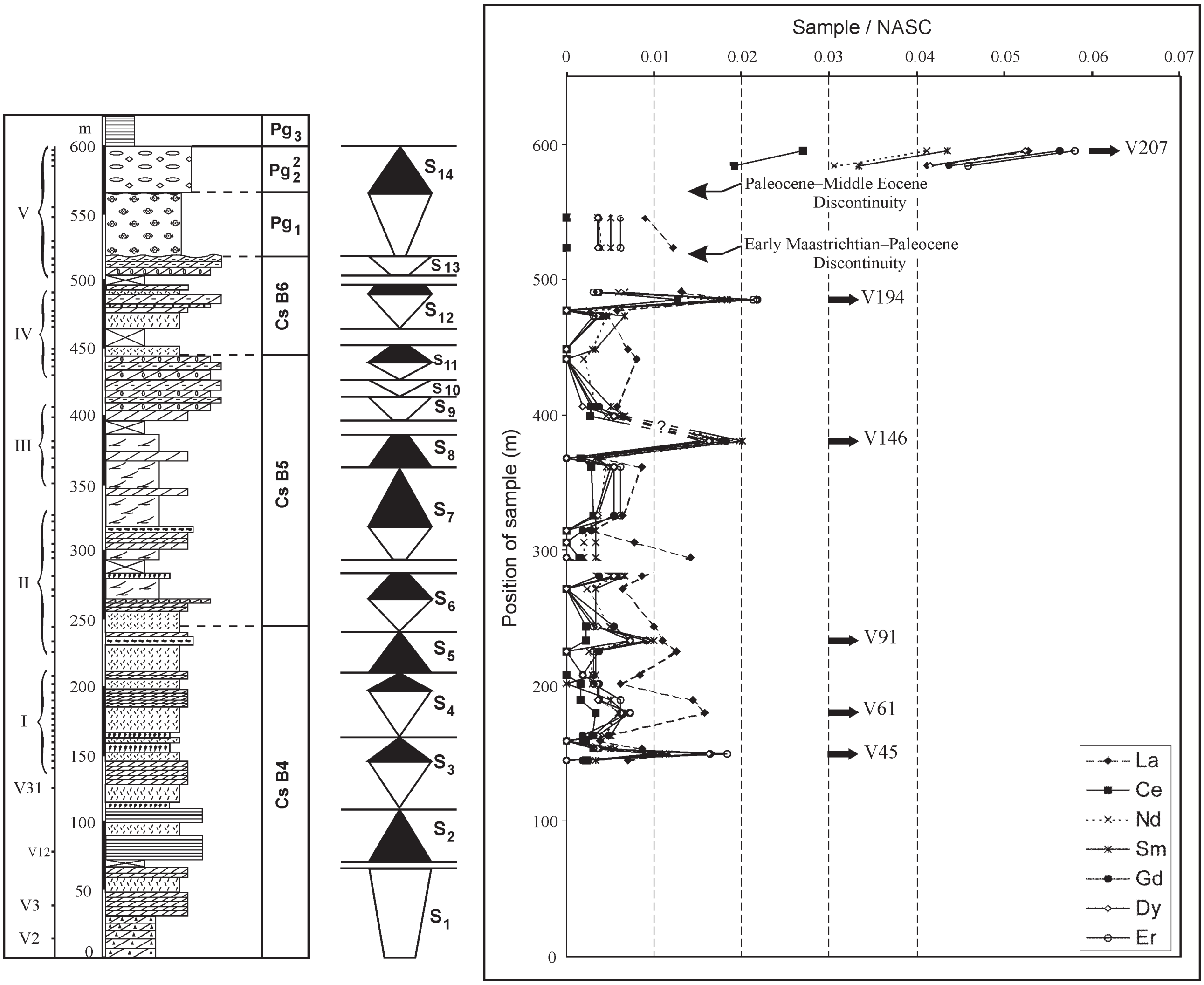

Fig. 7. Normalized Rare Earth Elements (REE) profiles for the L'Escalier section (Kruje-Dajt massif). Data are listed in Table 4. Legend: Fig. 2. Note: Solid arrows indicate positive geochemical tendency.

linity (Steuber & Veizer 2002). In carbonate platforms, a high Sr content reflects a more open marine environment located in the distal part of a depositional profile and, inversely, a low Sr content is indicative of a low salinity environment near subaerially exposed islands, located in the proximal part of the same profile (Vincent et al. 2006). As a matter of fact, in both sections of the Kruja Platform, petrographic observation did not allow us to find any kind of evaporite precipitation (crystals or ghost crystals of gypsum or anhydrite). The highest contents of Sr (765.25 and 1016.68 ppm, Table 2) in the L'Escalier section (samples V204 and V207, Fig. 5) are associated with nummulites and discocyclines limestones (facies 11) of Middle Eocene age (Heba & Prichonnet 2006): this is new evidence reflecting open marine conditions with normal salinity and characterizing more distal depositional environment of facies 11 (Fig. 2). In contrast, the low Sr contents recorded by the same facies in the La Route section and by all proximal depositional environments (facies 1 to 9) which characterize the Upper Cretaceous carbonates in the two sections may indicate the influence of meteoric water (low salinity) due to the decrease in paleobathymetry and the exposure related to early diagenesis, and the effects of burial diagenesis (Vincent et al. 1997, 2006), as discussed in section 5.1.

Normalized REE variations are more significant in the L'Escalier section (Fig. 7) than in the La Route section. The highest values (black arrows, samples V45, V91, V146, V194 and V207) correspond to the retrogradational parasequence set (sequences S3, S5, S8, S12, S14) and suggest a series of short and more important detrital inputs that characterize transgressive systems tracts. However, some anomalies are observed during the regressive episodes of three sequences: high REE values in the sequence S4 (sample V61); and high lanthanum values in the sequences S7 (sample V110) and S11 (sample V178). These deviations from the predicted relationships suggest perturbations in the local clay input included in the insoluble fraction of calcimeter analyses which has been controlled in 4 samples, showing proportions of up to 12 % of insoluble material (Figs. 3 and 4): samples V173, V187, M73 and M136.

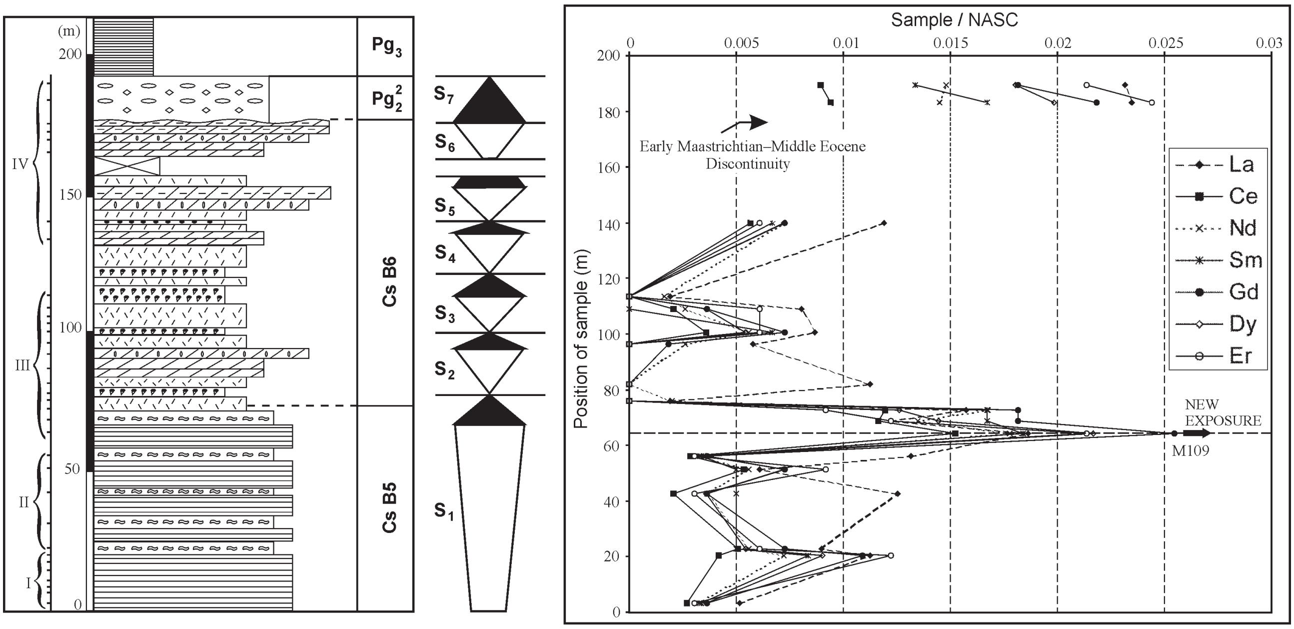

Fig. 8. Normalized Rare Earth Elements (REE) profiles for the La Route section (Makareshi massif). Data are listed in Table 4. Legend: Figs. 2 and 8.

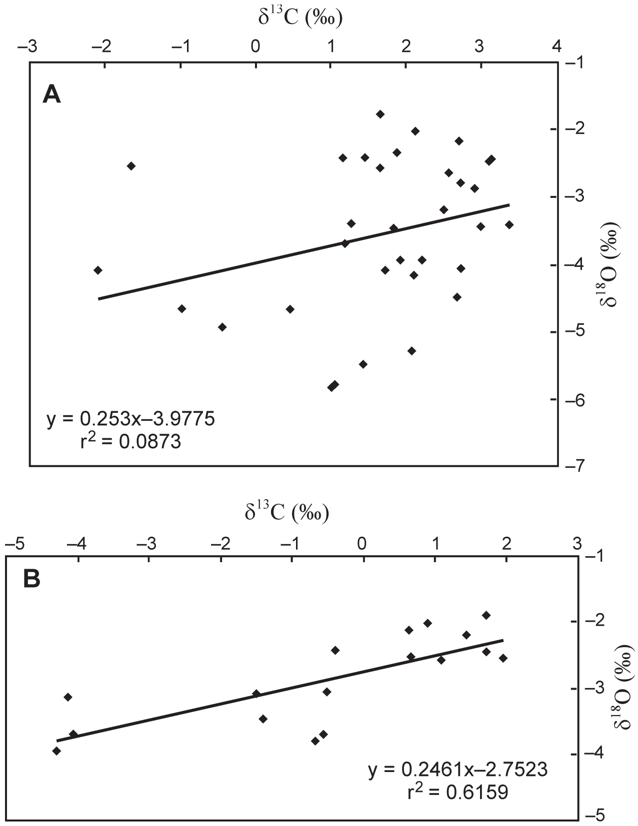

Fig. 9. Cross-plot of $\delta^{13}C$ and $\delta^{18}O$ values of measured bulk sediment samples for: **A** — L'Escalier section (Kruje-Dajt massif); and **B** — La Route section (Makareshi massif). Regression analysis of $\delta^{13}C$ and $\delta^{18}O$ (thick lines), equations and correlation coefficients (r^2 values) are noted. Data are listed in Table 2.

In the two sections, peaks in dolomite content are isolated between the limestone facies. Several peaks correspond to the progradational set of genetic sequence: S2, S3 and S11 sequences in the L'Escalier section (Fig. 3); and S2, S4 and S6 sequences in the La Route section (Fig. 4). Moreover, near the top of these sections, the dolomite increase (samples V203 in L'Escalier and M210 in La Route) coincides with the major regression in the Kruja Platform at the end of the Early Maastrichtian time recorded in the S13 and S6 sequences, which include essentially upper intertidal to supratidal environments (facies 7 and 8, Fig. 2). Finally, in the L'Escalier section, two peaks in dolomite content (samples V2 and V3, Fig. 3) are associated with dolomite facies, such as brecciated dolomites (facies 9) and bioturbated dolomite (facies 5). This distribution of high values in the dolomite content in both sections supports the sebkha-type dolomitization in a very shallow environment (Heba & Prichonnet 2006).

Conclusions

The study of the geochemical signatures together with sedimentological data of shallow-water carbonates of Late Cretaceous and Paleocene to Middle Eocene age from the L'Escalier (Kruje-Dajt massif) and La Route (Makareshi massif) sections, Kruja Platform (Albania), supports the following conclusions:

1 — The depleted values in strontium contents (most of them, from 200 to 400 ppm), the homogeneous $\delta^{18}O$ values (between –2.90 ‰ and –3.56 ‰) in the two sections and the significant covariation between $\delta^{13}C$ and $\delta^{18}O$ in the La Route section reflect the development of a regional meteoric phase and associated carbonate diagenesis. Consequently, the initial marine chemical signal is modified during the diagenesis de-

veloped near subaerial-exposed sedimentary environments. Petrographic analyses support these results;

2 — The geochemical patterns suggest a new exposure level during the Late Cretaceous time, at the CsB5/CsB6 biostratigraphic limit. In the L'Escalier section, this exposure recorded by sample V178 is identified by the end of the low Sr values and by the negative excursions of $\delta^{13}C$ and $\delta^{18}O$ values. In the La Route section, the exposure level recorded by sample M109 is characterized by the low Sr values and by the low $\delta^{13}C$ and $\delta^{18}O$ values, and the positive peak of normalized REE values. This subaerial exposure, at the end of the regressive phase of the S11 sequence (L'Escalier section) and the S1 sequence (La Route section), is comparable to that recognized by the decrease of strontium isotope values of rudist shells in the Island of Brač (Apulia domain). It could correspond to the global sea-level reported from the Boreal Realm, North Atlantic and the southern Tethyan margin;

3 — The high Sr content in samples V204 (780 ppm) and V207 (1016 ppm) in Middle Eocene carbonates (facies 11, nummulites and discocyclines limestones) at the L'Escalier section probably reflects a more distal part of the Kruja Platform during this time, in a normal open marine environment;

4 — Elevated values for REE in both sections coincide with maximum water depths during the transgression episode. Anomalies in REE concentrations during regressive episodes in sequences S4, S7 and S11 in the La Route section suggest local perturbations possibly linked with a small increase in clay content, but more data would be necessary to decipher the exact origin of these changes;

5 — The increase in dolomite contents (55–86 %) corresponds to the regressive episodes in genetic sequences and dolomitic facies, suggesting a sebkha-type dolomitization as explained by the sedimentological analysis.

The geochemical characterization therefore appears to be a useful approach to complete the general environment of platform sedimentation in an emersion context. A comparison of these results with data from equivalent platforms in the Apulia domain would be of interest.

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