CHAPITRE II

CARACTÉRISATION GÉOCHIMIQUE DES CARBONATES DE LA PARTIE ORIENTALE DE LA PLATE–FORME :

METEORIC DIAGENESIS OF LATE CRETACEOUS AND PALAEOCENE–EOCENE SHALLOW-WATER CARBONATES IN THE KRUJA PLATFORM (ALBANIA): GEOCHEMICAL EVIDENCE

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2.1 RÉSUMÉ

Des analyses géochimiques [la calcimètrie, la teneur en Sr, les variations isotopiques du $\delta^{13}C$ et $\delta^{18}O$ et les variations de Terres Rares (REE)] associées à l'analyse sédimentologique et séquentielle sont effectuées sur les coupes de L'Escalier (massif de Kruje-Dajt) et de La Route (massif de Makareshi). Ces deux coupes représentent une série carbonatée d'âge Crétacé terminal à Éocène de la plate-forme de Kruja (Albanie), qui appartient à la marge passive d'Apulie.

Les faibles valeurs du Sr et les valeurs homogènes du $\delta^{18}O$ dans les deux coupes ainsi que le synchronisme entre les valeurs du $\delta^{13}C$ et $\delta^{18}O$ (coupe de La Route) sont attribués à une diagenèse précoce, également démontrée par l'analyse pétrographique.

Au passage des biozones CsB5-CsB6, les pics et les excursions négatifs des valeurs de Sr et les excursions négatives du $\delta^{13}C$ et $\delta^{18}O$ dans les deux coupes, ainsi que le pic positif des REE (coupe de la Route), ont permis de mettre en évidence une nouvelle émersion durant le Crétacé supérieur : celle-ci est également reconnue au Campanien moyen (77.3 Ma), dans la plate-forme carbonatée de l'Ile de Brač (partie d'Apulie), grâce à la chute des valeurs isotopiques du Sr des rudistes. Cette émersion généralisée supra-régionale est liée à une baisse du niveau marin eustatique au Campanien moyen, enregistrée aussi dans le Domaine Boréal, dans l'Atlantique nord de l'époque et dans la marge méridionale de la Téthys.

Cette évidence géochimique les résultats de l'analyse sédimentologique et suggère un maximum de régression (baisse du niveau marin relatif) au passage des biozones CsB5-CsB6. Les fortes valeurs du Sr pour les calcaires de l'Éocène moyen (coupe de l'Escalier) indiquent un changement de milieu qui passe d'un lagon à un milieu marin ouvert. Les pics positifs des REE correspondent aux maximums d'approfondissement (transgressions), caractérisés par une augmentation relative de l'apport détritique. Cependant, les anomalies de certaines valeurs suggèrent des perturbations à caractère local, liées aux changements des apports argileux et aux modifications causées par la diagenèse. L'augmentation du pourcentage de la dolomite correspond aux épisodes régressifs, aux tendances régressives et aux faciès dolomitiques intertidaux à supratidaux.

2.1 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 Late Cretaceous (CsB4, CsB5, CsB6 biozones) and Palaeocene to Middle Eocene shallow-water carbonates that crop out at Kruje-Dajt massif (L'Escalier section) and Makareshi massif (La Route section).

The low values in Sr content, 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-buffered 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 sedimentological analysis and suggests a maximum regression (a sea-level fall) at the transition between 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 track, characterized by small increase of detrital input. However, anomalies of certain values in both sections suggest disturbances linked either to changes in clay input and to diagenetic modifications. Peaks in dolomite content are linked with regressive episodes, or regression tendency, and dolomitic facies, as indicated by intertidal-supratidal depositional environments.

2.2 INTRODUCTION

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

Trace elements and carbon isotope stratigraphy realised in pelagic and hemipelagic carbonate successions combined with sedimentological analyse 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 and 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 palaeoenvironments, the palaeosalinity and the influences of the diagenesis, particularly important in these sediments (Vincent et al., 1997, 2004).

The water-rock interaction of the diagentic 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, showing often high-amplitude fluctuations because of the diagenetic overprint which complicates the identification of 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 (Vincent et al., 1997, 2004; Joachimski, 1994; Buonocunto et al., 2002).

This study presents geochemical data for the Late Cretaceous and Palaeocene to Middle Eocene carbonates of Kruja platform, a folded and overthrust zone which is recognized from South to North in Albania (Papa, 1970; I.S.P.GJ. and I.GJ.N., 1983; Meço and Aliaj, 2000; Robertson and Shallo, 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, described in Heba and 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 analyzed for carbonates, strontium and stable isotope ($\delta^{13}C$ and $\delta^{18}O$) content, and Rare Earth Elements (REE). The two sections presented here are the same than in the Heba and 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.

2.3 GEOLOGICAL SETTING

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

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

The stratigraphic succession is dominated by Late Cretaceous neritic carbonates, limestones and dolomites, containing benthic foraminifera that were deposited in a confined subtidal to supratidal environment (Papa, 1970; Peza, 1973, 1975, 1977, 1982; I.S.P.GJ. and I.GJ..N., 1983; Heba, 1997; Meço and Aliaj, 2000; Robertson and Shallo, 2000; Heba and 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 Cretaceous and Early Eocene times, with also some differences between the two sections. The major regression in Kruja platform began at the end of the Early Maastrichian and extended for about 3 Ma at the L'Escalier section, where CsB7 foraminifera biozone (Upper Maastrichtian) is missing (Heba, 1997; Heba and Prichonnet, 2006), and about 20.5 Ma at the La Route section creating a gap ranging from biozone CsB7 to the Early Eocene. Evidently these gaps include largely the Cretaceous-Tertiary limit. The second regression is characterized by the presence of bauxite, but is only observed in the L'Escalier section: it lasted about 5 Ma during the Early Eocene. At the top of carbonate sequence in both sections, the Middle Eocene consists of organogenic limestones, deposited in an open shallow subtidal environment.

2.4 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 can be found in Heba and Prichonnet (2006).

The Late Cretaceous to Palaeogene carbonate deposits of L'Escalier and La Route sections display eleven sedimentary facies (F1 to F11; Fig. 2), ranging from subtidal to supratidal environments. Those 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 foraminifera (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 a dolomitization during the early diagenesis in a sabkha-type supratidal environment (Purser, 1980; Walker and James, 2000; Heba and Prichonnet, 2006).

According to the depositional model of facies succession seven distinctive parasequences have been identified (Heba and 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 both 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 (Upper Campanian-Early Maastrichtian), (Heba and Prichonnet, 2006).

Similar episodes of regression associated with continental diagenesis or sedimentation (karstic fillings) are reported since 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, Gusic and Jelaska, 1990). 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.

2.5 GEOCHEMICAL APPROACH

2.5.1 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 applied on all 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).

Stable isotopes, Sr 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 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 analysis (Table 3) were obtained at OGS GeoLabs in Sudbury (Ontario) with an ICP-MS (IM-100) unit for samples prepared by 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.

2.5.2 Description of geochemical variations

Calcimeter measurements

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

In the L'Escalier section (Table 1), where 60 % of 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 % limestone, 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 CsB6 biozone, respectively to 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 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; Palaeocene 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 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 Late 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 (sampleV194). Thus, over most of biozones CsB4 and CsB5, $\delta^{13}C$ values remain around 2‰. After a long-term decrease until the top of 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). Tertiary limestones are characterized by $\delta^{13}C$ values near +1.1‰.

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 CsB5 biozone (at the level of V178 sample), followed by a sharp positive shift. 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 and 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 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 as 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) 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 elements (REE) measurements

In the L'Escalier section (Fig. 7), normalized REE values of the Late Cretaceous and the Palaeocene 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 CsB5 biozone.

2.6 INTERPRETATION OF GEOCHEMICAL VARIATIONS AND DISCUSSION

2.6.1 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 to 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 and Veizer, 2002). Similar depleted values (ranging from 200 to 400 ppm) have been reported in the Bajocian-Bathonien 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 in calcite matrix, partially recrystallized; (b) early to more late 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 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 and 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. 9-B) that is indicative of a clear diagenetic alteration, and a minor covariation for the L'Escalier section (Fig. 9-A), 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 with 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 with 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 Escalier section and near the level of sample M109 in the La Route section. 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 S1 cycle (genetic sequence).

2.6.2 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 progradational parasequence set of S11 cycle (Heba and 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 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 and Prichonnet, 2006): this event registered near a transgressive surface coincides with the inflection point between the progradational parasequence set of S1 cycle (intertidal environment, facies 1 and 2, Fig. 2) and the facies 5 which indicates relatively greater environment of deposition (subtidal).

In the two sections, these subaerial events are registered at the same stratigraphic position, between biozones CsB5 (Early Campanian) and CsB6 (Upper 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 CsB5 sedimentation in the two sections was eustatically controlled and another maximum regression may have occurred at the transition between 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 salinity (Steuber and Veizer, 2002). In carbonate platforms, high Sr content reflects more open marine environment located in the distal part of a depositional profile and, inversely, low Sr content is indicative of 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 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 (Heba and Prichonnet, 2006): this is a 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 are common to the Late 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 retrogradational parasequences (sequences S3, S5, S8, S12, S14) and suggest a series of short and significant 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 indicated by the insoluble fraction of calcimeter analyses in 4 control samples, showing proportions of up to 12% of insoluble material (Figs. 3 and 4): samples V173, V187, M73 and M136.

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 Kruja platform at the end of Early Maastrichtian time recorded respectively on the S13 and S6 sequences, which include essentially upper intertidal to supratidal environments (facies 7 and 8, Fig. 2). Finally, in the 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 therefore supports the sabkha-type dolomitization in a very shallow environment (Heba and Prichonnet, 2006).

2.7 CONCLUSIONS

The study of the geochemical signatures together with sedimentological data of shallow-water carbonates of Late Cretaceous and Palaeocene to Middle Eocene from 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 developed near subaerial-exposed sedimentary environments. Petrographic analysis are supporting this 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 δ13C and δ18O values. In the La Route section, the exposure level recorded by sample M109 is

characterized by the low Sr values and by the low δ13C and δ18O values, and the positive peak of normalized REE values. This subaerial exposure, at the end of regressive phase of the S11 sequence (L'Escalier section) and S1 sequence (La Route section), is comparable with that recognized by the decreasing of strontium isotope values of rudist shells in the Island of Brač (Apulia domain). It could correspond with 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 (facies11, nummulites and discocyclines limestones) at the L'Escalier section reflects probably a more distal part of the Kruja platform during this time, in a normal open marine environment;

(4) Elevated values in 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 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 with 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.

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

Sample	% CaCO3	% (CaMg)CO3	Facies	Sample	% CaCO3	% (CaMg)CO3	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 Figures 3 and 4

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)	$\delta^{18}O$ (‰ VPDB)	Facies	Sample	Sr (ppm)	$\delta^{13}C$ (‰ VPDB)	$\delta^{18}O$ (‰ 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 Figures 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 (Knije-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 Figures 3 and 4

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 Figures 3 and 4

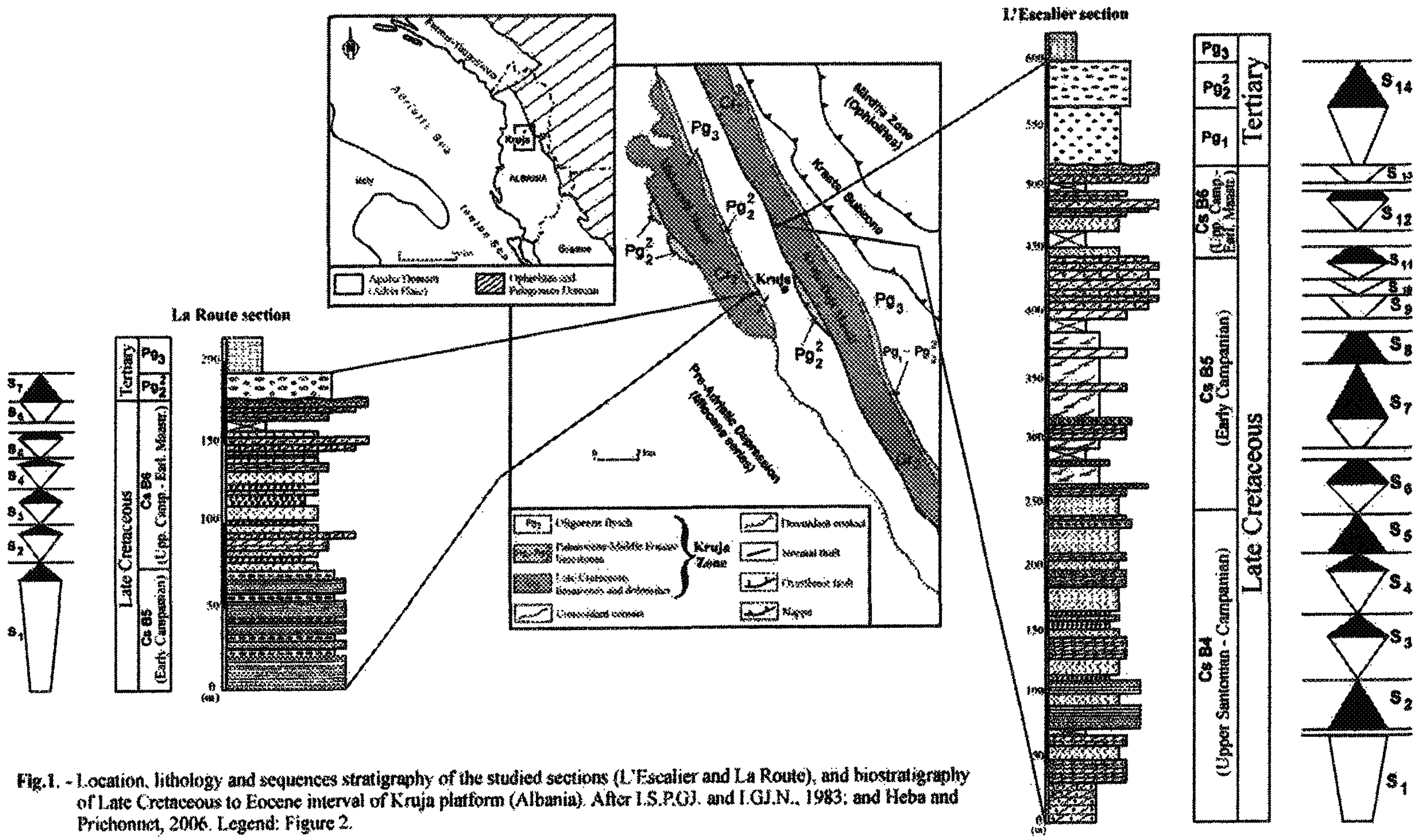


Fig.1. - Location, lithology and sequences stratigraphy of the studied sections (L'Escalier and La Route), and biostratigraphy of Late Cretaceous to Eocene interval of Kruja platform (Albania). After I.S.P.GJ. and I.GJ.N., 1983; and Heba and Prichonnet, 2006. Legend: Figure 2.

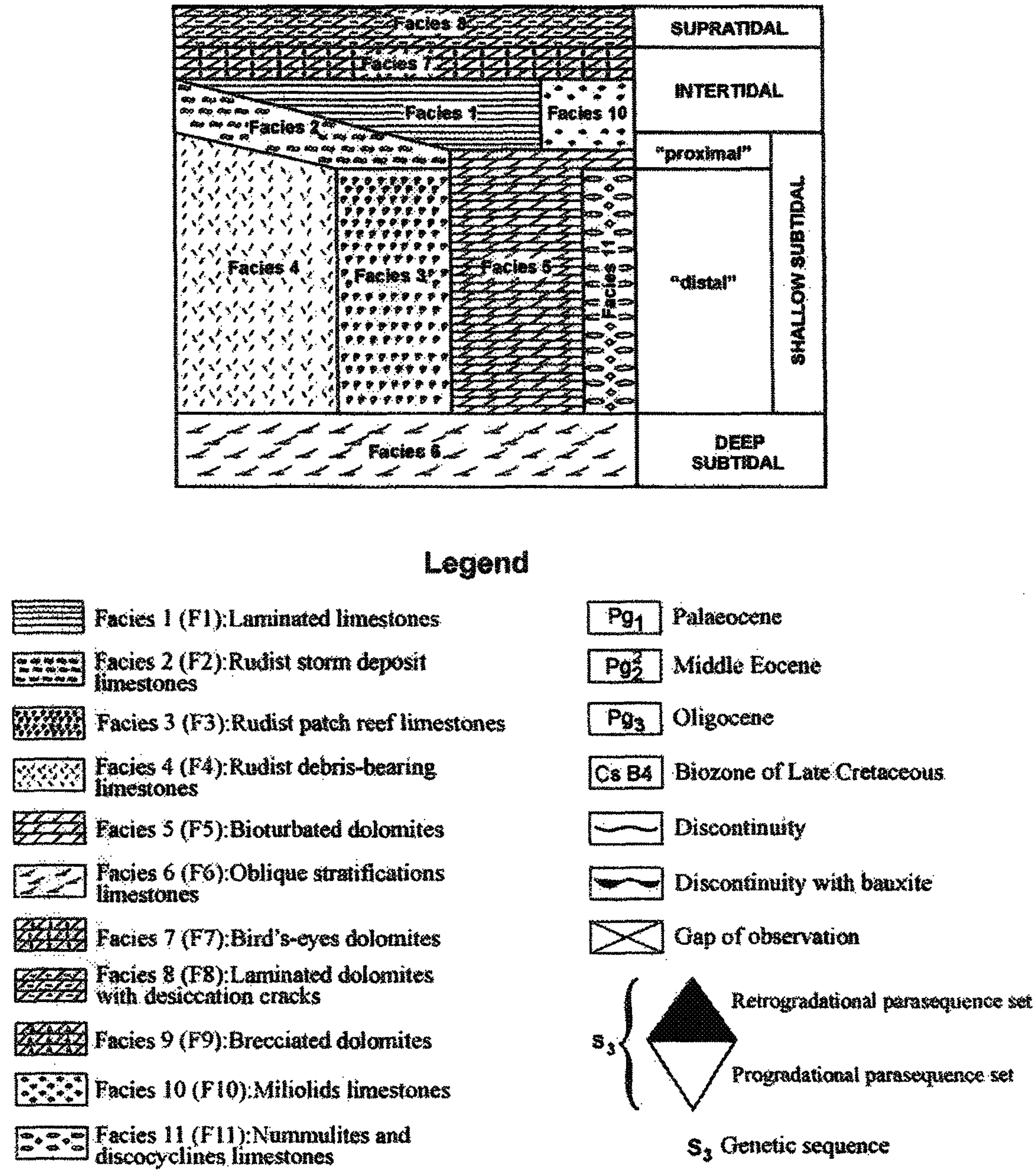


Fig.2. - Sedimentary depositional model of the facies succession (after Heba and Prichonnet, 2006) and legend key.

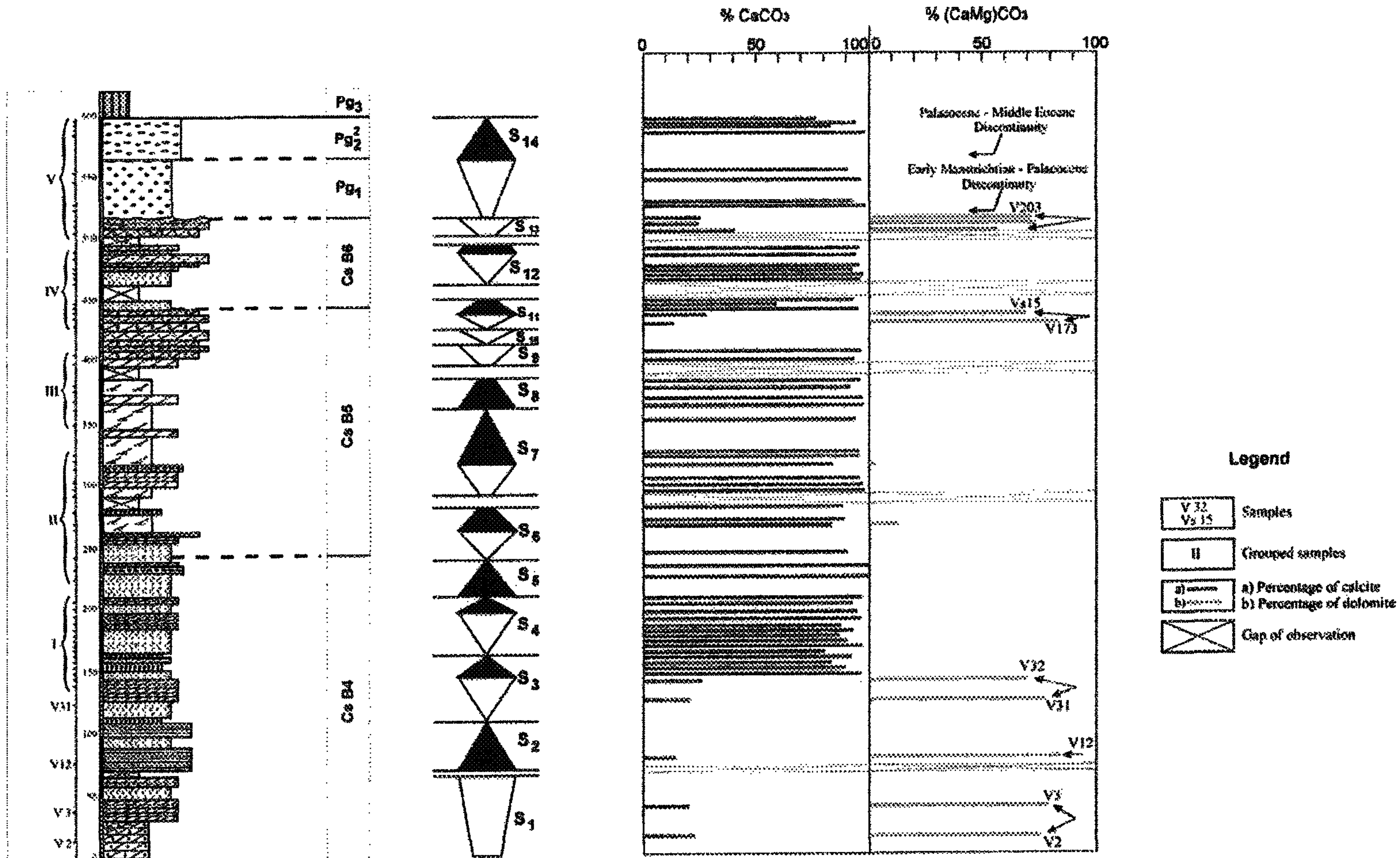


Fig.3. - Calcimetry profile for the L'Escalier section (Kruje-Dajt Massif). Data are listed in Table 1. Legend: Figure 2. Note: Stratigraphic position of grouped samples: I (V32, V36, V45, V54, V48, V51,V57, V58, V62, V64, V70, V74 to V76, V83); II (V88, V91, V96, V101, V102,V108, V110, V111, V114, V120, V124, V125); III (V134, V136, V143, V144, V146, V140, 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).

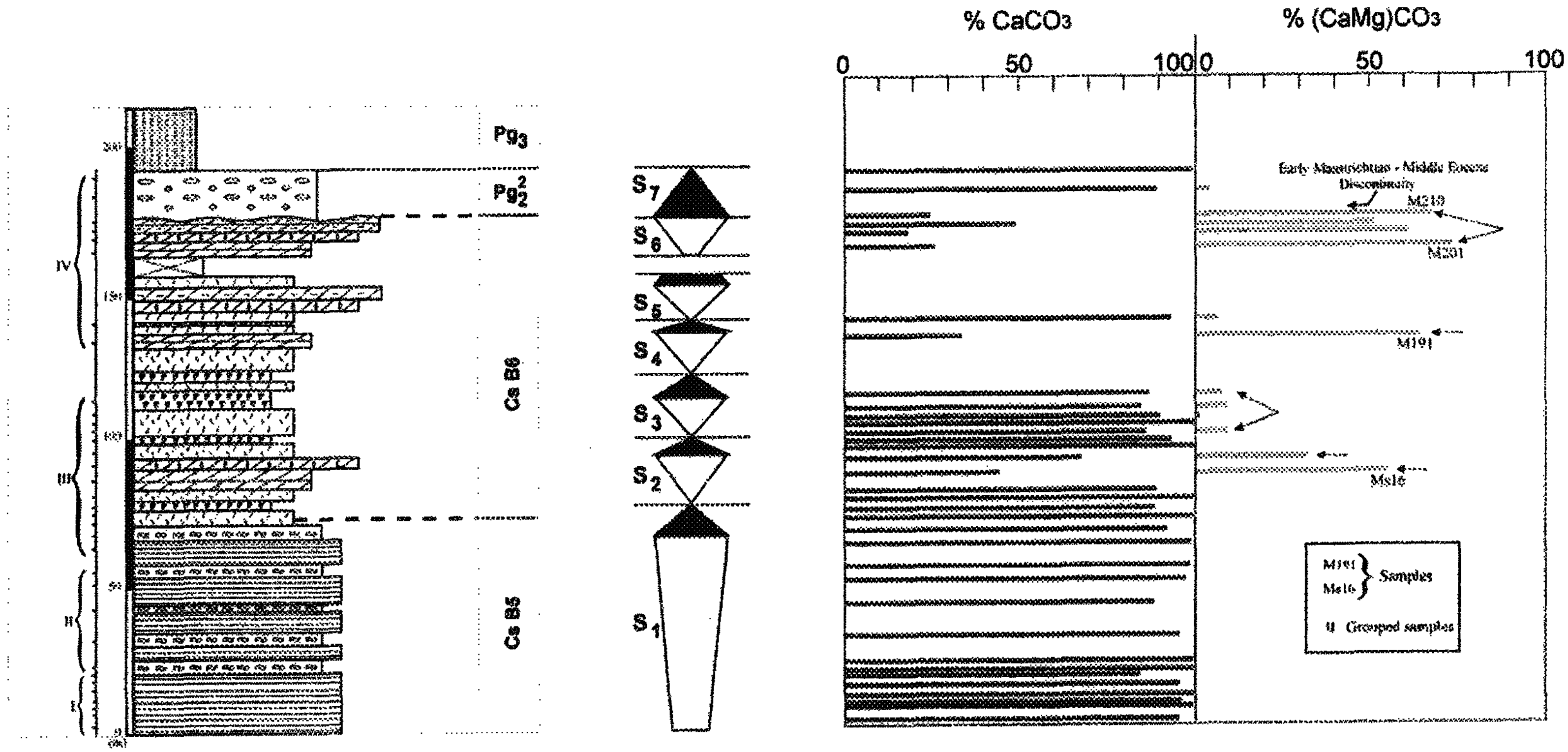


Fig.4 - Calcimetry profile for the La Route section (Makareshi Massif). Data are listed in Table 1. Legend: Figure 2. Note: Stratigraphic position of grouped samples: I (M10, M17, M20, M25, M35, M41, M46); II (M47, M73, M92, M99, M105); III (M109, M127, M129, M136, M142, M145, Ms16, M186, M186/1, M159,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

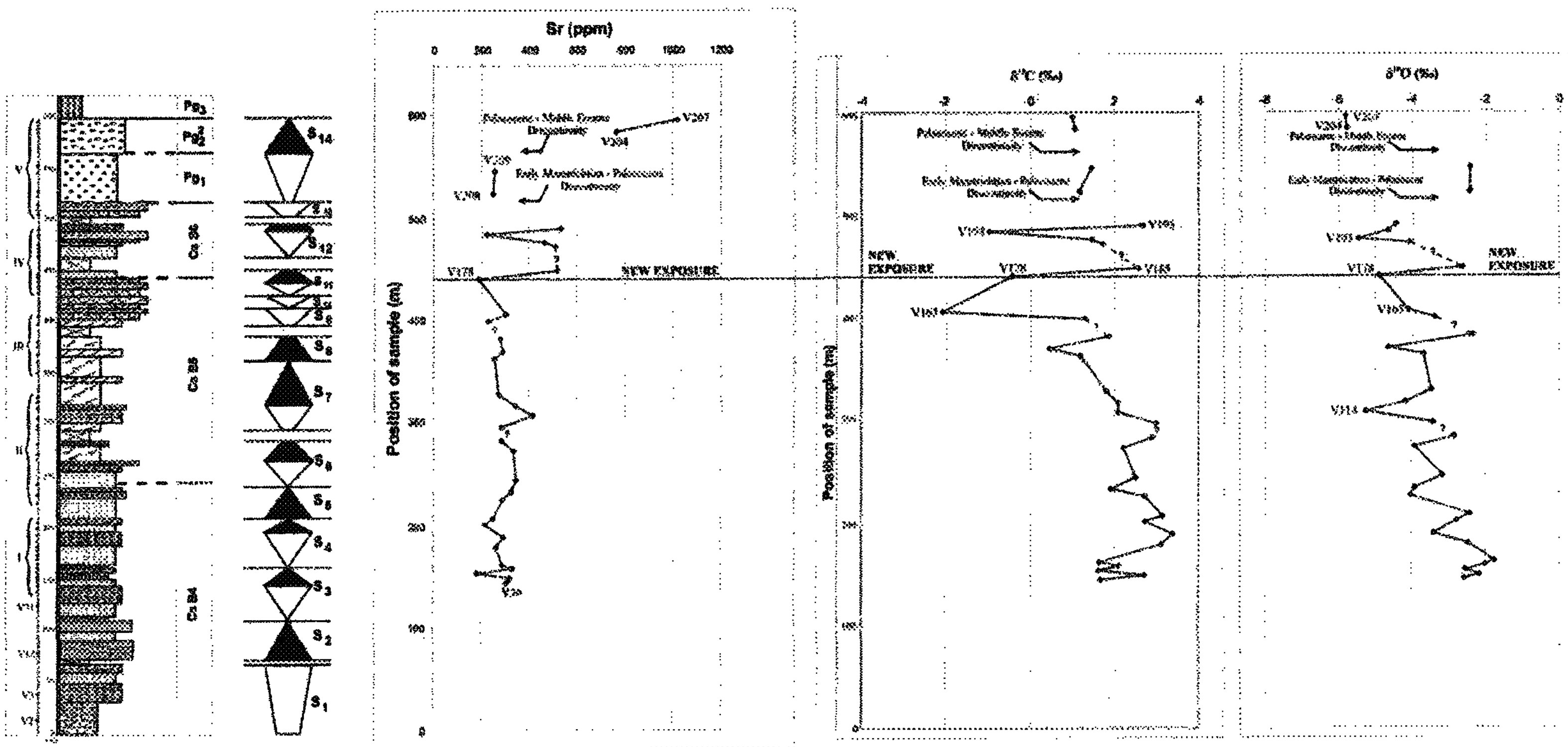


Fig.5. - Strontium and stable isotope profiles for the L'Escalier section (Kruja-Dajt Massif). Data are listed in Table 2. Legend: Figure 2.

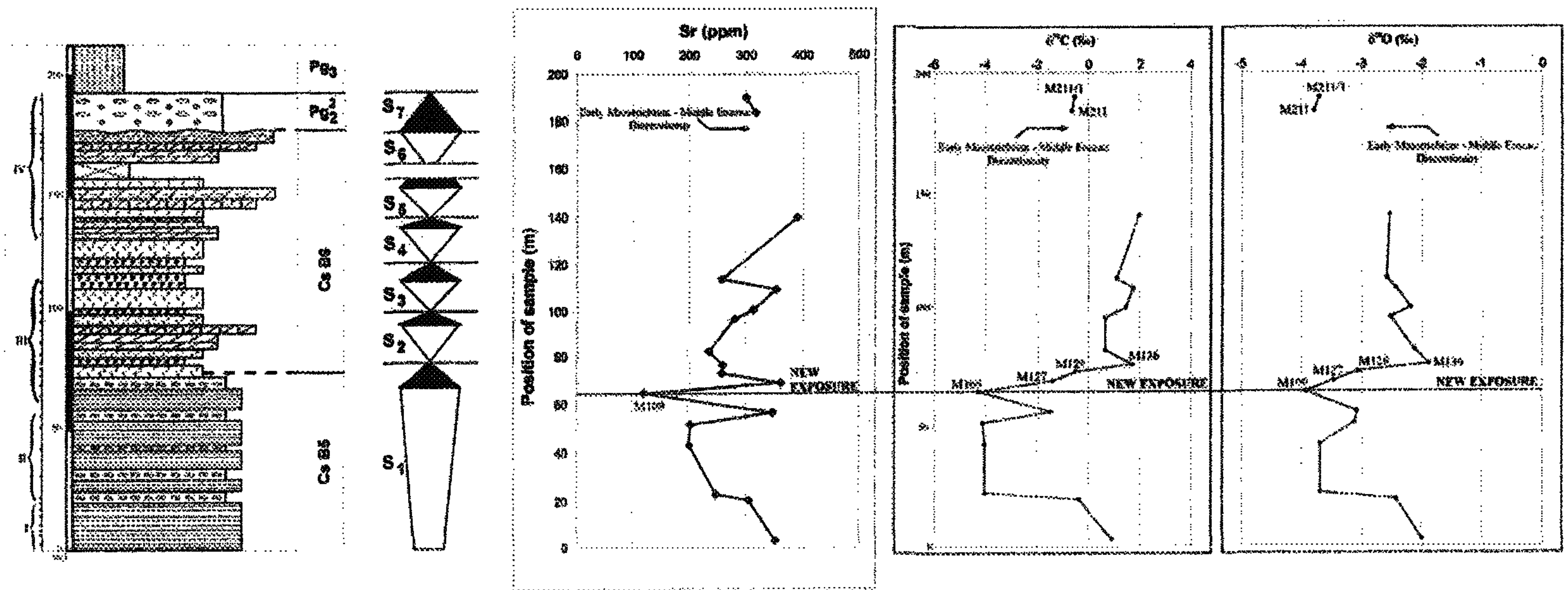


Fig.6. - Strontium and stable isotope profiles for the La Route section (Makareshi Massif). Data are listed in Table 2. Legend: Figure 2.

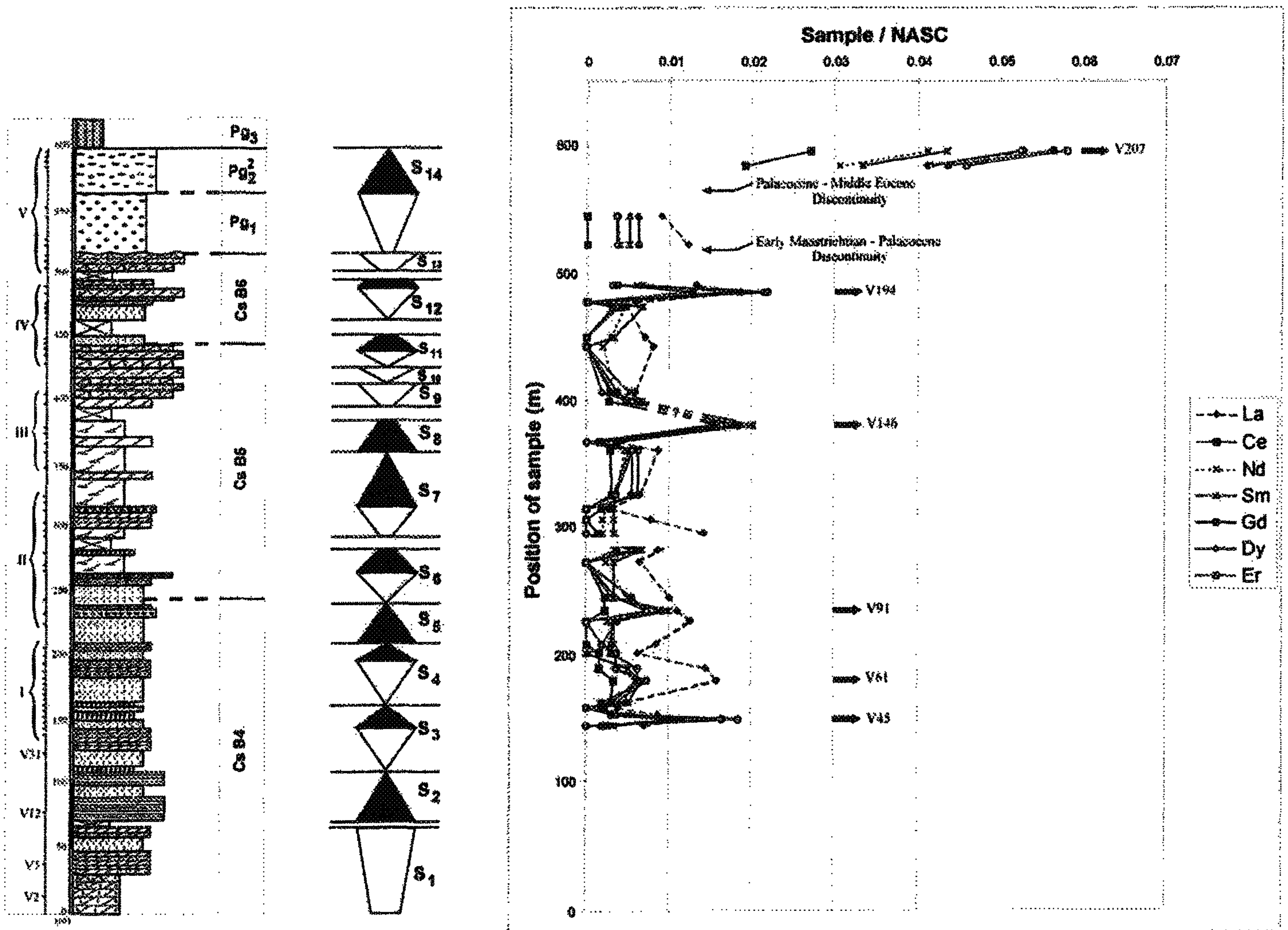


Fig.7. - Normalized Rare Earth Elements (REE) profiles for the L'Escalier section (Kruje-Dajt Massif). Data are listed in Table 4. Legend: Figure 2.
Note: Solid arrows indicate positive geochemical tendency.

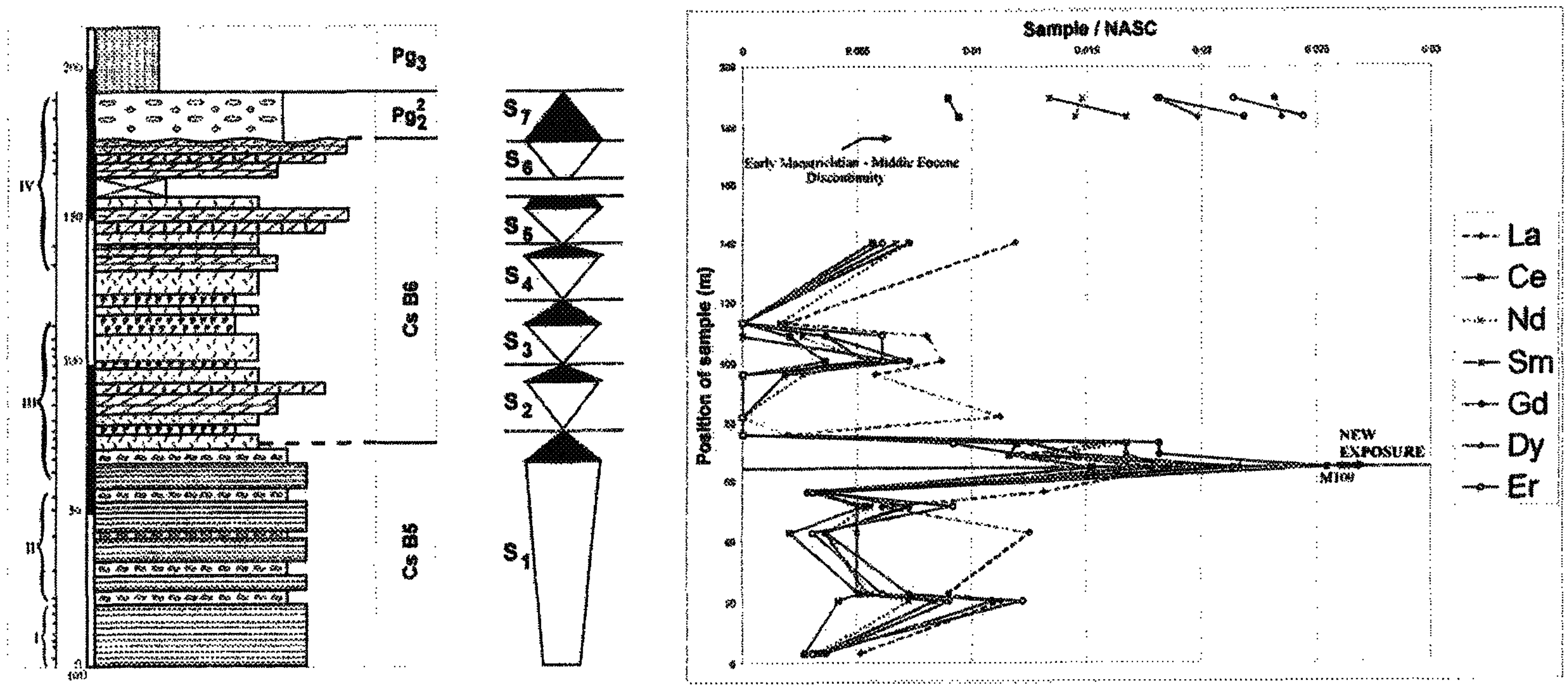
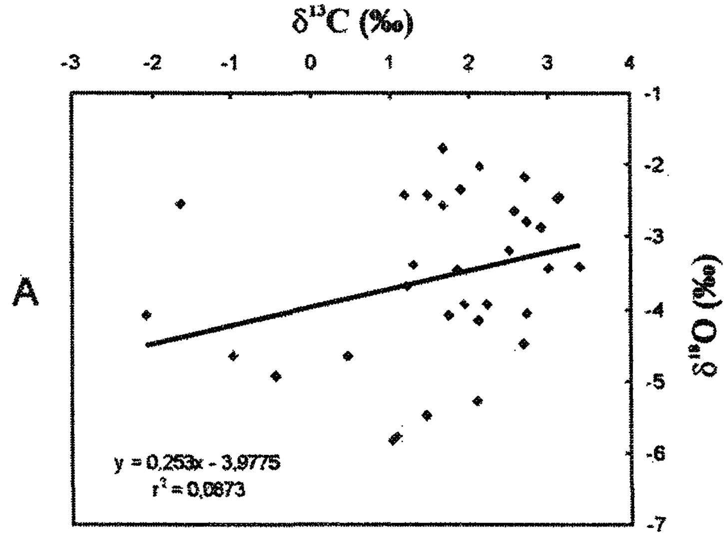


Fig.8. - Normalized Rare Earth Elements (REE) profiles for the La Route section (Makareshi Massif). Data are listed in Table 4. Legend: Figures 2 and 8.



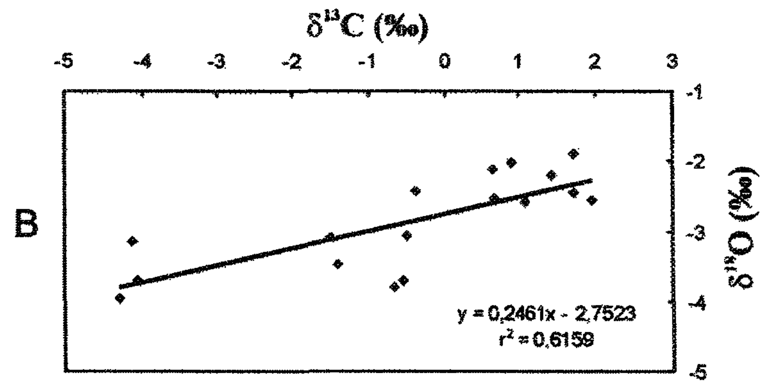


Fig.9. - Cross-plot of $\delta^{13}C$ and $\delta^{18}O$ values of measured bulk sediment samples for: A- L'Escalier section (Kruje-Dajt Massif); and B- La Route section (Makareshi Massif). Regression analysis of $\delta^{13}C$ and $\delta^{18}O$ (thick lines), equations and correlation coefficients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