SULPHUR PRESENCE IN PALEOKARST INFILLINGS AND BITUMEN SIGNS IN UPPER CRETACEOUS CARBONATES FROM THE KRUJA ZONE (ALBANIA)

Ana FOCIRO[1], Gjergji FOTO, Antea LINATOPI

UDC: 553.611.08:546.22(496.5)

SUMMARY

Kruja zone represents mainly shallow-water carbonate deposits (Cr_2-Pg_2). They consist of dolomites, limestones with rudists also rich in miliolides and textularides with frequent hiatus, emersions, discontinuity surfaces and even bauxitic horizons. This paper aid to provide some explanations about the origin of blue clays within paleokarst infillings, caverns and the presence of bitumen and their impact in the surrounding rocks in the region of Burizana in Makareshi anticline structure, Kruja zone. This area was previously known for oil exploration and several exploration wells were drilled, in the South-East, as Makareshi-1 well, while in the West, Ishem, a series of wells, all with the object of oil exploration in carbonate section from the surrounding structures. Also, in this region, the presence of Miocene transgression is present. The presence of terrigenous rocks in the highest hypsometric position, the intrusion of blue-grey clays between carbonate formation, the smell of sulphur in the blue clay formation and the bitumen signs in the cavities of the carbonate rocks are part of the present study.

Key words: Kruja zone, blue clays, sulphur, bitumen.

INTRODUCTION

In literature, paleokarst is defined as karst that has been buried by younger rocks. It is a common component of successions in which limestones are present and serves as a clear indicator of terrestrial environments and, to some extent, duration of emergence. Interpretation of paleokarst may be complicated by two factors; firstly, it is usually visible only in two, rather than three dimensions, and secondly, burial by younger rocks does not prevent modification or even destruction of the paleokarst by subsurface dissolution (Simms, 2014). Most paleokarst exposures are usually level with or are negative features in the landscape. If the materials filling ancient caves

[1] **Ana FOCIRO**, ana.fociro@fgjm.edu.al, Polytechnic University, Faculty of Geology and Mining, Department of Earth Sciences,
Address: Rruga e Elbasanit, Tirana, Albania, Tel. +355 42 375 246/5

or dolines are strong enough, paleokarst features can be preserved as positive features protruding above the general level of the land surface (Osborne 2013). After the construction of the new road, a new outcrop in the western part of the Makareshi structure was discovered. In the study area, the carbonate rocks suffered from syngenetic karstification and early-diagenetic near-surface karstification. The phenomenon of paleokarst was encountered throughout the entire section (Qorri, 2014). The infilling materials represent different types of terrigenous facies. In some cases, the blue clay (argillaceous) karstic infillings smell of sulphur. This paper concerns the terrigenous occurrence which was studied in this shallow marine carbonate successions exposed in Makareshi structure. This paper aims to better understand the presence of terrigenous rocks in the highest hypsometric position of the section, intrusion of blue-gray clays between terrigenous and carbonate formations, the origin of sulphur smell in the blue clay formation and the signs of bitumen in the cavities and cracks of the carbonate rocks.

GEOLOGICAL SETTING

The passive margin of the Apulian Plate during the Mesozoic and Palaeogene was bordered by extensive carbonate platforms, known in Albania as the Kruja zone or Kruja platform. The Kruja zone extends northward into the Adriatic Dinaric platform (Montenegro, Croatia) and southward into the Gavrovo platform (northern Greece). Based on different studies in Albania only upper Mesozoic - Palaeogene deposits are exposed. The Makareshi anticline structure is situated in the Kruja zone, part of external Albanides (Figure 1a). In the Borizana section, a section of the Makareshi structure, recently studied by Qorri (2016), the Campanian - Maastrichtian includes deposits of restricted and open platform interior limestones and dolomitic limestones intercalated by dolomites and terrigenous paleokarst infillings (Figure 1b). The Upper Cretaceous is marked by a major hiatus spanning the late Maastrichtian and continued to the early Eocene. Above this gap, the series continues with the middle Eocene bioclastic limestones, deposited in an open shallow subtidal environment. Above the limestones, the horizon of the upper Eocene “passing marl” marks the transition to the 1500 m thick succession of the Oligocene flysch (Heba and Prichonnet, 2006).

MATERIAL AND METHODS

Our study focuses on the Campanian – Maastcrichtian succession cropping out at the southwest of Kruja city and to the east of the Burizana village. The samples were collected from different outcrops along the section. The section consists of thick to medium bedded wackestones to packstones, commonly laminated, rudists biostromes, rudist floatstones/rudstone, solution collapse limestone breccias, dolomitized limestones, dedolomites and terrigenous formation (Figure 1b). The study was focused on the macroscopic description of the samples representing lithified and semi lithified sandstone and XRF analysis for blues clay formation, in order to obtain an overview regarding their chemical composition (Figure 2).

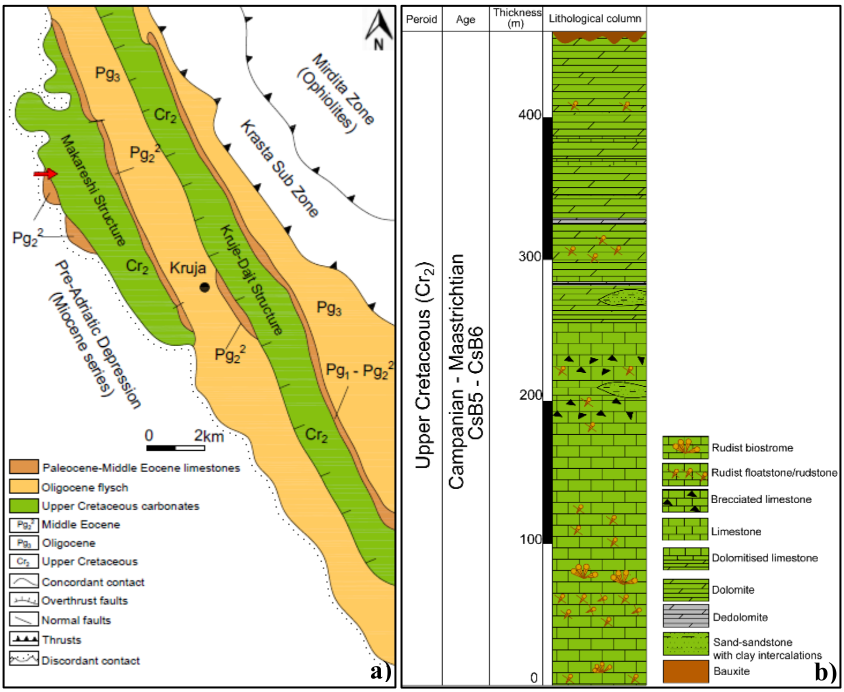

Figure 1: a) Simplified tectonic map showing locations of the Kruja zone, La Route section (after I.S.P.GJ and I.GJ.N., 1983). b) Lithologic column of Upper Cretaceous deposits from Burizana section (Qorri, 2016).

RESULTS AND DISCUSSIONS

From the field geological surveys conducted in the study area and from previous geological studies conducted in the region for oil and gas exploration, but also based on the geological map of the territory on a scale of 1: 200.000. We can state that some of the terrigenous rocks (not those associated with blue clays) are part of the transgressive series of Peri-Adriatic molasses. According to previous studies, they belong to the "Helmesi" formation on the north bank of the Droja River. The Pliocene formation overlies the Upper Cretaceous limestones.

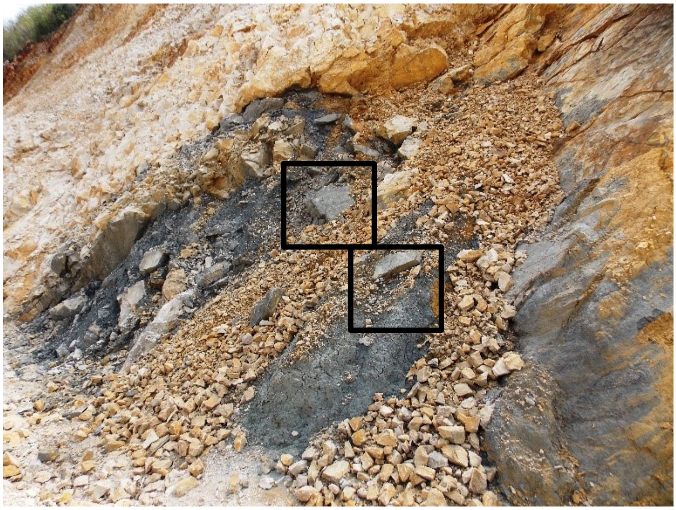

Figure 2: Blue clay infilling and sandstone blocks within this level (black rectangles).

Figure 3: Bitumen signs in limestone cracks.

From the bottom up, the base of the transgression is quite clear, which is often represented by large-grained quartz sandstones, pebbles with different mineralogical compositions, blocks and boulders of limestone. Determining the presence of terrigenous rocks, in this part of the Makaresh structure, is a new finding in the geology of this area and that moves toward the east the boundaries of the Miocene transgression drawn on the geological map of the scale 1: 200.000. The sandstones of the “Helmesi” formation are generally yellow to reddish. In this mixture of granulometry, carbonate blocks of various sizes and shapes are distinguished, and almost all lithological types are found in the fresh carbonate section, including carbonate blocks containing grey to blue organic matter. Limestones blocks, near or inside diluvium have a reddish colour due to the contact with soils rich in iron oxides. The intrusions of blue clays in Upper Cretaceous carbonate rocks and terrigenous formation don’t show any special morphology, but they look like leakage over carbonate surface. Macroscopic observations in fresh outcrops besides their characteristic colour show soft touch, high moisture and smell of sulphur. Based on the geological observations, blue clays within the carbonate section have to do with shapes that are compatible with the surrounding rocks, i.e., they do not appear to have formed in sedimentation conditions simultaneously with the carbonate rocks, i.e., are not of the same age. They fill paleokarst surfaces and other characteristic cavities formed in pure carbonate rocks (Figure 2). From the location, it seems to come from the younger upper levels. For the geological history this carbonate section, this mechanism is acceptable. Their entry paths within the carbonate section appear to be interconnected with cracks, fissures, caverns and cavities. To clarify the relation of the position of the blue clays with the entry paths in the carbonate section, as evidenced by the observations in the outcrops, below the bauxite level, the presence of cavities and caverns of considerable size is noticed, but also in lower parts of the section. On both sides of the road, there are formed two great sinkholes. It seems that the sinkholes have infill and distribute within the carbonate section those types of clays during frequent emersion of the shallow-water carbonates. The limestone presence with clear indicators of mud eating organism activity is one of the evidence of the shallowness of this carbonate substrate and the possibility of supplying the sinkholes with such clays. Also, according to Serjani (2014) the presence of blue clays in samples from well 5-13, with a depth of 83.5-99.5 m has been previously described. From the chemical analyses performed before, they result in high content of sulphur trioxide, reaching up to 12% SO_3. According to the literature from previous works, the blue clays are also found inside the molasses formations. The clearest presence of these compact blue rocks, within the terrigenous rocks, is evidenced in some channels in this territory. In the channels cross to the extension, starting from the deepest part, the base of transgression on the Cretaceous carbonates is identified, which is represented by sandstones. Irregularly distributed blue clays overlain the sandstones and above them, overlain the Quaternary diluvium. Their total thickness is about 20-25 meters. It is known that their origins are from the continent and are the result of the feldspars weathering supplied by the eastern tectonic zones. According to the literature (Bentor, YK and M. Kastner, 1965; Buckley, et al.1978), these clays, claystone and marls with blue or grey-blue colour, are layered silicates such as glauconite. As it appears from the comparisons between cases 1 and 2 of the literature, in the case of Burizana clays, the water content is missing, which would normally reach about 10%, which also completes the total content (Referring to the above-mentioned authors, in the two wells DH/14 and DH/ 13 it is also noticed that at the bottom of these blue clays and rocks, there are strong cavities and caverns, the preferred place of placement of these formations. Changes in the values of sulphur trioxide content are observed towards the increase, depending on their location whether they are on perforated surfaces or at open or uncovered depths (in wells). There is also a change in the reduction of sulphur trioxide content from soft and wet surface clays (formed at relatively younger ages) to rocky clay-carbonate mixtures (formed earlier and compacted), therefore, vary depending on the time of formation. Also, changes in the values of trioxide content in the same samples were determined from the analytical analysis. After the initial determination of SO_3 content, it comes down. The explanation for these low values of the molasses may come from the fact that they are in contact with sandstones with sufficient porosity and permeability to retain sulphur trioxide but also to carry it to the surface and unlike depth clay bodies within the carbonate section which have no contact with the surface or are completely blocked except cavities, cracks, tectonic faults which can cause degassing.

Table 1). According to L. Montanari, these clays that are often called blue, in addition to Italy, are also found in Malta and are aged from the upper Langhian to the lower Tortonian (L. Montanari, 1987). So, the origin of these formations, such as those within the carbonates but also in the molasses section, we would say that during the formation of carbonate sediments, there was a connection of the Cretaceous Sea with the continent through areas with the limited temporary or partial circulation with the sea and consequently to the basin. Glauconitic clays have intruded, which, as has been proved, come from the destruction of the feldspar rocks of the eastern zones. These clay muds, formed during all geological times, occupy karst cavities and caverns, undergo to lithogenesis and chemical-physical diagenetic processes, forming a mixture of carbonate and clay material. This supply process has continued even in the later Pliocene times while the carbonate formation has undergone erosion and weathering by reshaping cavities and karsts that are filled with the same clay mud but in this case, they have not reached the stage of lithogenesis and have remained unconsolidated appearing as soft crumbly and hygroscopic rocks. The blue clay rock blocks, already within the section, may have a two-way source either originating from the continuous weathering of Cretaceous carbonate rocks or directly from the eastern part of the continent supplying the crumbly and clayey material. According to mineralogical-petrographic studies carried out in this territory, it results that even in recent times, after the formation of the carbonate formation, the flysch formation of the Lower Oligocene (Pg_3^1) overlain them. These deposits belong to the upper part of the quartz-quarzitic zone and the lower part of the glauconite-phosphate zone (Meçaj 1992). As presented above, their distribution and quantity in both carbonate and molasses sections cannot be predicted by general geological works. The peculiarity of blue clays, as we mentioned, is the strong smell of sulphur and the presence of sulphur trioxide (SO_3) confirmed through chemical analysis. Sulphur trioxide is a chemical component. In gaseous form, this substance is a pollutant, as it is the primary substance of acid rain. It is an anhydride that produces mostly H_2SO_4 (sulphuric acid) through the following reaction:

$$SO_3 \text{ (gas)} + H_2O \text{ (liquid)} \rightarrow H_2SO_4 \text{ (acid)} \ (\Delta H_f = -88 \text{ kJ mol}^{-1})$$

The reaction occurs quickly and with extra energy from outside, but can also hardly be produced in quantity. At temperatures above 340 °C, sulphuric acid, sulphur trioxide and water are found in equilibrium concentrations. In our study area, in the carbonate section of the Upper Cretaceous, even according to macroscopic observations the bituminous limestone horizons are distinguished. They are easily distinguishable by the dark grey concerning the colour of the surrounding rocks. In closer view the presence of fresh or even dry bitumen that saturates the cracks of the rocks are visible (Figure 3). Geochemical studies have also identified this fact (Çurri et al., 1990). The conditions of their formation are known. Generally, they require the accumulation of organic matter mixing with carbonate material mainly of the mudstone type, which creates the possibility of its protection from the destructive action of oxygen or bacteria. These conditions are met in a reducing environment. The immersion of this potential layer is to be oil-formed, at depths where the temperature reaches the stage of catagenesis. At this stage, diagenesis gas is formed, and subsequently, oil formation. The amount of oil formed in this way will depend on the residence time of this potential layer in the oil window. The maximum immersion and reaching the required temperatures occurred during the Lower Oligocene period, where the basin, together with the territory in question, underwent the greatest possible immersion. According to the data and studies performed, folding of this area occurred after the Lower Oligocene and in this case, the cooking conditions of the organic matter were stopped (Çurri et al., 1990, Prifti et al., 2013). The carbonate succession, more or less, has been and is under the direct influence of hydrocarbons with the highest molecular weight. There are mostly asphaltene and resins and practically oxides of heavy metals such as vanadium, nickel, nitrogen, sulphur, carbon dioxide, etc. According to the same geochemical study (Prifti et al., 2013) the oils of Upper Cretaceous limestones and Miocene sandstones of the "Tirana-Ishëm" Depression, which are found at some shallow depths, are heavy and biodegraded oils. There is a close association between the bituminous limestones and all the other rocks within the Upper Cretaceous carbonate section in the study area, but also between this section and the terrigenous formations that overlay the carbonates. The whole carbonate section has undergone a strong peneplanation, the effect of strong movements during folding after the Lower Oligocene, then shifts from East to West, overthrusts of the eastern part of the structure over its western part, until its complete covering up. Folding during and especially after the Pliocene have made its gradual immersion to the West thus being included by an influx of the sea from North-West to South-East, through a transgressive series expressed by the unconformity of Tortonian formations and then, the most powerful immersion during the Pliocene, whose boundaries extend as far as the area in question. The active geologic history has made the connection of the whole section through cracks, faults with relatively small amplitude, through intensive karst development, etc., made this section disperse its contents, including bitumen. It is precisely this contact of limestone horizons with bitumen that supplies hydrocarbons and their content to all kinds of clays including glauconite clays. In general, clays are molecular structures with many free molecular radicals that absorb and retain almost two times their volume in water, or as the case may be, with other chemical elements that feed on bituminous sections, including sulphur. In addition, the gradual immersion of the Makareshi limestone toward the West, in addition to direct contact with seawater, has led to the formation waters, accompanied by bituminous horizons, rich in hydrocarbon elements and especially sulphur (Bilaj) (Frashëri et al., 2010), which may have been here as well, have brought the sulphur content in the glauconite clays. Regarding the higher SO_3 content, in addition to the relation with lithology and bitumen content, the same relation is observed with the content of Al_2O_3 and Fe_2O_3, over (0.2-0.6) %, which exceeds almost 10 times the general background not exceeding 0.07%. In three cases the high content of TiO_2 up to 22 % is distinguished and that is directly related to bituminous limestones, while in some cases it reaches 32 % and is associated with marl limestones. Within the carbonate section, as we have explained above, there are two types of rocks, grey and blue. One type is associated with grey-blue clays, quite wet and with a strong sulphur smell that has leaked down and the second type, shapeless intrusions; unspecified extensions within compact carbonate rocks. They have not been analysed for chemical and mineralogical composition but based on the above relations; they result in high SO_3 content that reaches maximum values of up to 7%. According to Foto et al., (2015) the samples taken and studied for the mineralogical and chemical composition of the rocks in the wells, show that these phenomena observed on the surface exist in-depth as well. Thus, in two of them (DH 5/14 and DH.5/ 13), are found the clays with the blue colour (blue-clays) in separate intervals but also horizontal continuity up to ten linear meters (Serjani 2014). Referring to the above-mentioned authors, in the two wells DH/14 and DH/ 13 it is also noticed that at the bottom of these blue clays and rocks, there are strong cavities and caverns, the preferred place of placement of these formations. Changes in the values of sulphur trioxide content are observed towards the increase, depending on their location whether they are on perforated surfaces or at open or uncovered depths (in wells). There is also a change in the reduction of sulphur trioxide content from soft and wet surface clays (formed at relatively younger ages) to rocky clay-carbonate mixtures (formed earlier and compacted), therefore, vary depending on the time of formation. Also, changes in the values of trioxide content in the same samples were determined from the analytical analysis. After the initial determination of SO_3 content, it comes down. The explanation for these low values of the molasses may come from the fact that they are in contact with sandstones with sufficient porosity and permeability to retain sulphur trioxide but also to carry it to the surface and unlike depth clay bodies within the carbonate section which have no contact with the surface or are completely blocked except cavities, cracks, tectonic faults which can cause degassing.

Table 1: Chemical composition of glauconite.

Chemical composition	Whare Flat, Otago, New Zealand	Makhtesh Ramon, Israel	Well 5-14, Burizanë
SiO_2	49.29	46.52	61.48
TiO_2	0.12	-	1.08
Al_2O_3	3.17	4.61	15.10
Fe_2O_3	21.72	24.76	7.03
FeO	3.19	2.02	-

MgO	3.85	4.65	1,13
CaO	0.74	0.51	2
Na_2O	0.12	0.19	0.22
K_2O	6.02	7.65	2.01
H_2O^+	7.21	5.83	-
H_2O^-	4.60	3.20	-
P_2O_5	0.32	0.08	0,135
SO_3	-	-	1.5
Total	**100.35**	**100.02**	**90.875**

CONCLUSIONS

Regarding the origin and the occurrence of terrigenous formations (sandstones, blue-clays, carbonate blocks and reddish soils) it is clear that these formations are remnants of the transgressive molasses nappe that lies in the West and Northwest of the Burizana region, part of Tirana-Ishëm Depression. The blue clays and the gray-blue rocks, in the two rock formations, those within the carbonate succession and molasses, we would say are glauconitic clays, which as it has been proven, come from the weathering of the eastern zones. These clay muds occupy karst cavities, pits and undergo lithogenesis and chemical-physical diagenetic processes, forming a mixture of carbonate and clay material. This sediment supply process has continued even in the later Pliocene while the carbonate formation has undergone erosion and weathering forming new cavities and karsts surfaces that are filled with the same clay mud but in this case, they have not reached the stage of lithogenesis and have remained unconsolidated appearing as soft and hygroscopic rocks. Authigenic minerals present in clayey sediments are calcite and dolomite, pyrite, kaolinite, opal and chalcedony, glauconite, sericite and illite. According to mineralogical-petrographic studies carried out in this territory, it results that even in recent times, after the formation of the carbonate formation, is overlain by the Lower Oligocene flysch formation. These deposits belong to the upper part of the quartz-quartzite zone and the lower part of the glauconite-phosphate zone. The major problem associated with the presence of blue clays is the high content of sulphur trioxide, SO_3. We can say that the sources of sulfide content are first of all related to the high content of organic matter present in the carbonate section which at certain moments has passed to the stage of diagenesis and catagenesis from which the respective bitumens were formed. The sources have also stimulated the formation and the removal of fluids that have accompanied the formation of bitumen in the upper part of the section, towards lower pressures, thus being captured by glauconitic clays, ready to fill free radicals or to replace water connections with SO_2 sulphur gases. The second possible source is the continuous movement of groundwater accompanying the organic matter, and possibly also the high-temperature thermal waters found in the springs of Mamurras and Ishem (Ishmi 1/b well). Bacterial action is also a possible source. Regardless of the source, this chemical element is already present in the section, whether carbonate or molasses and predictable for SO_3 content.

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