Characteristics, origin and hydrocarbon potential of the Upper Cretaceous Source Rock in the Rio Muni Basin, Equatorial Guinea

Jiang Zhao¹,²*, Jun Cao ³ and Ning-ning Zhong ³

¹ Key Laboratory of Earthquake Early warning, Institute of Seismology, CEA, Wuhan 430071, China
² Hubei Earthquake Agency, Wuhan 430071, China
³ State Key Laboratory of Petroleum Resources and Prospecting, China University of Petroleum, Beijing 102249, China

*Corresponding author’s e-mail: 863388711@qq.com

Abstract. In order to study the geochemical characteristics, origin and its hydrocarbon potential of the Upper Cretaceous marine source rocks in the Rio Muni Basin, Equatorial Guinea, 62 debris samples of the Anduak-1 well in the Rio Muni Basin were collected to Rock-Eval pyrolysis, whole rock organic petrology analysis. This study revealed that the OM in the upper Cretaceous source rock is early mature - mature, with moderate abundance and fair quality (mainly type II and III). The organic matter has a mixed marine–terrestrial origin and deposited in the marine environment, the plant debris were probably suffered from a long-distance transportation via fluvial or else forces. The main hydrocarbon generation phase of the type III kerogen was more duration than type II, initial hydrocarbon generation was earlier, and ending hydrocarbon generation time was late. Comprehensive studies demonstrated that it has a good hydrocarbon potential to the upper Cretaceous marine shale, and is an unneglectable hydrocarbon source rock.

1. Introduction
Rio Muni Basin has been overlooked by the industry for much of the last decades, however, the Ceiba oil field was discovered by Triton until 1999, it establishes a new high-potential oil play in this part of the Gulf of Guinea [¹]. Rio Muni Basin is one of the series of genetically related rift-drift salt basins—Aptian Salt Basins. The primary sources of these Salt basins are either pre-salt rift phase lacustrine shales or younger Cenomanian to Eocene drift phase marine shales, only the primary source intervals of the Rio Muni Basin, was the Albian organic rich micrites. Dailly (2000) noted that the uppermost part of the Aptian and lower part of Albian sequence have organic rich mudstones "with excellent source potential". The Matondo 1, Benito 1 and East Eviondo 1 wells penetrated up to 200 m of Aptian-Albian source rock. The source facies was lacustrine to restricted marine of Type II/III kerogen, with TOC values of 2-4% and Hydrogen Index of 200-500 mg HC/g TOC. Ross & Hempstead consider the organic shales of the Upper Aptian saliferous sequence as the main source rocks in the basin [²]. Turner (1995) states that these shales have mainly algal organic matter with up to 6% TOC and over 20 mg HC/rock Hydrocarbon potential (S2) in the Benito 1 well. All of these studies previous suggested that the primary source rock are Aptian-Albian intervals in the Rio Muni Basin. This is in markedly contrast to the other West African Aptian Salt basins. However, the recently new drilling
indicates that there is rich organic matter shale in the upper Cretaceous intervals, which has not been reported before.

This article focuses on evaluation of the upper rich organic matter sediments including Turonian, Santonian, Coniacian, and Campanian-Maastrichtian organic-rich shale, the organic matter (OM) origins discussing by organic petrography, the characteristics and mechanism of the different types of kerogen in the upper Cretaceous shales used by the thermal model experiments and petrolMod software.

2. Geological Setting
Rio Muni Basin is isolated from the North Gabon basin to the south, the Douala basin of Cameroon to the north[3]. The tectono-stratigraphic evolution of the basin can be divided into a number of separate phases. To date, no wells have penetrated strata older than middle to late Aptian and clear definition of the nature and age of an early rifting or transtensional phase is lacking. There are differential subsidence of possible early to mid Aptian age. It is overlain by a thick, upper Aptian continental/lacustrine succession followed by Albian-Cenomanian marine section. Following the onset of postrift subsidence, the Albian-Cenomanian sequence was locally deformed into a series of rafts that detach on a basal Albian, organic rich claystone section. Further deformation by Santonian-Coniacian transpression caused uplift of the shelf area and deposition of an Upper Cretaceous slope fan sequence. This is overlain by a Tertiary passive margin wedge [3-4] (Figure 1).

Table 1. Overview of activation energies and frequency factors for selected samples

| NO. | Depth(m) | Age          | Lithology | TOC (%) | Kerogen type | Activation energy(kcal/mol) | Frequency factor (s⁻¹) |
|-----|----------|--------------|-----------|---------|--------------|----------------------------|------------------------|
| A12 | 2977-2980| Camp.-Maas.  | Shale     | 1.31    | II₂          | 179.7-256.2                | 1.67E+17               |
| A19 | 3118-3121| Santonian    | Shale     | 1.16    | II₂          | 179.7-259.2                | 1.44E+17               |
| A30 | 3352-3355| Coniacian    | Shale     | 0.89    | III          | 183.9-280.1                | 1.24E+17               |
| A56 | 3922-3925| Turonian     | Shale     | 1.11    | II₁          | 179.7-246.6                | 1.43E+17               |

Figure 1. The stratigraphic chart of the Rio Muni Basin, Equatorial Guinea (modified after IHS data base, 2009)
3. Samples and experiments
For Maceral identification, 18 samples were embedded respectively in an epoxy resin and a section perpendicular to bedding was polished according to the procedure described by Amijaya and Littke (2006) and Taylor et al. (1998). Maceral measurements were obtained with a Leica 4500D light microscope, at the SKL of Petroleum Resource and Prospecting. The polished blocks were investigated at a magnification of 500× or 200× in incident white light and in incident light fluorescence mode, excited by ultraviolet (UV) and violet light.

The thermal simulation experiment of kerogen generation hydrocarbon in an open system was made in Petroleum Geochemistry Laboratory, Wuxi Geology Research Institute. Different kerogen types of 4 samples (one for type II1, two for type II2, one for type III (listed in table 1)) were chosen to be analyzed by Rock Eval-Six C036 Sartorius T008 device, each sample was respectively weighed three parallel samples, about 100mg. According to various heating rate (5, 15, and 25°C/min) for starting heating temperature of 300°C, final temperature of 600°C, the heating temperature and the product quantity were recorded during the heating process, according to these recording data, we get the Temperature - Transformation rate curve, which is used for calibration of the kinetic parameters.

4. Results and discussion

4.1. Rock–Eval pyrolysis
Pyrolysis data indicate that abundance of organic matter varied from 0.65-2.24% with an average 1.03% in the Upper Cretaceous shale interval, HI ranges from 68-467 mg HC/g Corg., Average 174 mg HC/g Corg., S1 + S2 values range from 0.52 - 5.78 mg HC/g Corg., mean 2.12 mg HC/g Corg.. The variation of pyrolysis parameters (HI, OI and S1 + S2) of Turonian shale are the largest range of variation in the entire Upper Cretaceous shale interval, HI distribution range: 68-467 mg HC/g Corg., OI: 116-423 mg HC/g Corg., S1 + S2: 0.83-5.51 mg HC/g Corg., reflecting the diversity and complexity of the organic matter in the Turonian shale.

There is a change from poor to good distribution of the organic matter abundance of the upper Cretaceous marine shale geochemical profile in the Anduak-1 well (Figure 2). The variation of organic matter abundance has a decreasing trend gradually from Campanian-Maastrichtian to Coniacian, while a increase trend gradually from the Coniacian to the Turonian. It has a relatively high abundance of organic matter of Campanian - Maastrichtian and Turonian in the entire upper Cretaceous shale interval. It is the minimum abundance of organic matter in the Coniacian shale. The longitudinal variation of HI values and S1 + S2 values has a great similarity with TOC values, reflecting the differentiation of organic enrichment and preservation in the Upper Cretaceous intervals.
Figure 2. Geochemical log of the upper Cretaceous source rock of Anduak-1 well in the Rio Muni Basin

There are mainly kerogen type II and III in term of the crossplot of HI-Tmax in the upper Cretaceous samples (Figure 3). Among them, type III are presented only in the Turonian samples, the rest of the Campanian–Maastrichtian, Santonian, Coniacian samples mainly kerogen type II and III, furthermore, type II accounted for overwhelming majority of the upper Cretaceous samples, indicated that the upper Cretaceous shales had potential for oil or gas generation.

The vitrinite reflectance being considered to be the most reliable and commonly used maturity indicator \(^5\text{6}\), An overview of maturity distribution was provided by VRr data. This maturity was confirmed by the observation of fluorescing liptinite macerals in UV light. Ro values for the Campanian-Maastrichtian samples ranged between 0.46% and 0.53% (Figure 3 and Appendix 1), indicating immature to early mature OM. Ro values for the Santonian samples is in the range of 0.49-0.56%, thus suggesting early mature, Coniacian samples showed a Ro value of 0.56-0.72%, indicating early mature OM. Ro values for the Turonian samples samples ranged between 0.68% and 1.07%, indicating moderate mature. There is a increasing trend of the maturity of the upper Cretaceous shale with the burial depth increasing.

On the basis of the analysis above, we can conclude that organic matter abundance, type and maturity of the Turonian shale samples, are all the best in the Upper Cretaceous marine intervals, which has a good potential of generation hydrocarbon as the Upper Cretaceous source rocks.
Figure 3. The crossplot of Tmax vs. HI of the upper Cretaceous marine source rock in the Rio Muni Basin

4.2. Organic petrography
There are variation of the maceral in the Turonian samples. Except for a large number of rounding vitrodetrinite, inertodetrinite and liptodetrinite are observed(Figure 4f), a smaller proportion of particles of alginate (Dinoflagellates) of marine origin was also observed (Fig. 4g), which indicates low input of marine-derived material in the Rio Muni Basin during Turonian times. A fecal-pellet-like particles also can be observed in Turonian samples(Figure 4h), which indicated of a bathyal or abysmal sea depositional environment.

Similar characteristics were found for the Coniacian, Santonian and Campanian-Maastrichtian samples, in which a number of rounding/regular vitrodetrinite, inertodetrinite and liptodetrinite was observed. The vast majority of the OM was classified as vitrinite and inertinite (Figure 4a, c, d, e), with some alginate and mineral-bituminous groundmass present (Figure 4b). The dominant liptinite group was liptodetrinite and bituminite, while alginite/amalginate were rarely observed. In marine sediments, alginate and liptodetrinite, represent the preserved remains of marine plankton. Bituminite is commonly regarded as a microbial degradation product of more labile OM that can only be (partly) preserved under specific conditions such as anoxic bottom waters [7].

Palynofacies analysis indicates a strong predominance of inertodetrinite, vitrodetrinite, and liptodetrinite in the upper Cretaceous samples, which account for about 70% - 95% of the total particles. These maceral particles can be classified into two main groups. The first group is composed of a large number of vitrinite, inertinite, exinite, which are derived from terrigenous higher plants. The second group is represented by alginite generally derived from marine plankton. Variations in maceral appearance not only highlight the origin of the OM (marine vs. terrestrial), but also the role of the depositional setting (i.e. intensity of oxidation). From another perspective, there were no intact cellular structures of higher plants well preserved, except for the sporinite partly preserved intactly through the diagenetic alteration. The shape of these inertodetrinite, vitrodetrinite, and liptodetrinite for the whole upper Cretaceous samples were presented high psephicity, partly angular. These maceral features above indicated that the plant debris were probably suffered from a long-distance transportation via fluival process or else forces on the basis of the area geological setting.
Figure 4. Microscopic observations in reflected white light (a, d, e, and f) and incident light fluorescence mode (b, c, g, and h); a, vitrinite, 50× 2759-2762m Campanian-Maastrichtian; b, Alginite, lipitodetrinite, mineral-bituminous groundmass, 50× 2800-2803m Campanian-Maastrichtian; c, sporinite 50× 2860-2863m Campanian-Maastrichtian; d, Inertodetrinite 20× 3238-3241m Santonian; e, Vitroodetrinite 50× 3370-3373m Coniacian; f, Vitroodetrinite, pyrite, 50× 3736-3739m Turonian; g, Alginite, 50× 3877-3880m Turonian; h, Fecal-pellet-like, 20× 4036-4039m Turonian.

5. Conclusion
The Cretaceous source rock of Anduak-1 well in Rio Muni basin is early mature to mature, with moderate OM abundance (TOC: 0.6-2.24%, 1.03% on average) and a good quality (mainly type II and III) to constitute a potential source rock.
The organic matter has a mixed marine-terrestrial origin and deposited in the marine environment, the plant debris were probably suffered from a long-distance transportation via fluvial or else forces. Above all, it has a good hydrocarbon potential to the upper Cretaceous marine shale. Especially the Turonian shale is an unneglectable hydrocarbon source rock.

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