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Organic Geochemistry of Tanjero Formation at Dokan and Shaqlawa, Northern Iraq

Mohamed W. Alkhafaji[1] , Salam I. Al-Jubouri[2]

[1] *Applied Geology Department, College of Science, University of Tikrit, Tikrit, Iraq*
[2] *North Oil Company, Kirkuk, Iraq*

ABSTRACT

Late Campanian - Maastrichtian Tanjero Formation at Dokan and Shaqlawa areas was studied to determine its hydrocarbon-generation potential and depositional environment conditions. For this purpose, seventeen samples were subjected for Total Organic Carbon (TOC) and Rock-Eval pyrolyis analyses. Bitumen was extracted from three samples and analyzed by GC-FID.

Generally, TOC and S2 values of Tanjero Formation are low (0.07-0.54 and 0.01-0.53; respectively); indicating they have low potentiality for hydrocarbon generation. Rock-Eval pyrolysis parameters (hydrogen index, oxygen index, and Tmax) indicate that the Tanjero Formation clastics contain mainly type IV and III kerogen. Pristane/phytane values indicate that the Tanjero Formation was deposited under oxic environment. Weathering (especially oxidation) reduced the TOC, the potentiality of the formation rock, and the Extractable Organic Matter (EOM) values.

Key Words: Tanjero Formation, Hydrocarbon generation, Oxidation

Introduction

Late Campanian-Maastrichtian Tanjero Formation consists mainly of clastic sediments (represented by marl, siltstone, sandstone, shale, and conglomerate) in addition to some limestone beds (Jassim and Buday, 2006a; Karim and Surdashy, 2006; Aqrawi et al., 2010). These clastic sediments were formed as flysh deposits in rapidly subsiding basin. At type section in Sirwan Valley, southeast Sulaimaniya, it divided into two parts: the lower part consists of 484 m thick of basinal marl, with some beds of limestone and siltstone beds; whereas the upper part comprising of alternating bedding of silty marls, siltstone, conglomerates, and detrital limestone with thickness up to 2010 m. however, it becomes thinly bedded and finer grained southwestward. Tanjero Formation is restricted to Balambo-Tanjero Zone and some parts of the Low Folded Zone of the Unstable Shelf. In these areas, it is widely exposed; sometimes it fills the synclines troughs between the anticlines (Sissakian et al., 2016). In Dokan area, the formation divided by Abdel-Kireem, (1986) into three units. Lower unit composed of alternating bedding of marl, siltstone, and fine sandstone with thickness about 460m. Middle unit represented by 209 m of chalky marl; whereas the upper unit is consisting of sandy limestone, shales, and sandstone with thickness of 124 m. Karim and Surdashy, (2016) suggested that the lower part of the formation represent lowstand system tract (mostly lowstand wedge) deposited in deep environment. The thin beds of marly limestone of the middle part at Dokan area represents transgressive system tract (TST). Highstand system tract (HST) is relatively thin (about 130 m).

Lower boundary of Tanjero Formation is conformable and gradational with Shiranish Formation; while the upper boundary is unconformable with the Kolosh Formation.

Tanjero Formation has been intensively studied by Abdel-Kireem, 1986; Karim and Surdashy, 2006; Al-Zubaidi, 2016; and Sissakian et al., 2016. Most of these studies focused on sedimentology, paleontology, stratigraphy, and geochemistry of the Tanjero Formation. There is no study dealt with the organic geochemistry of the formation; therefore, this study aims to investigate the organic geochemistry of this formation.

Geological Setting:

The study area is located in High Folded Zone of the Unstable Shelf. This zone is strongly affected by Cretaceous and Tertiary deformation. Limestones of the Mesozoic units occupy the anticline cores; whereas limestones and clastic of Tertiary units are in the flanks. The anticlines of this zone have a trend with NW-SE in northeast Iraq and changes to E-W in north Iraq (Jassim and Buday, 2006b).

During Late Campanian-Maastrichtian, major marine transgression occurred; this transgression was due to the closure of the Neo-Tethys. The obduction of ophiolite and closure of Neo-Tethys led to formation NW-SE extensional basins. When the obducted sheets of ophiolite were elevated above sea level, they were subjected to erosion and deposited in subsiding foredeep basin as flysh deposits represented by Tanjero Formation. Therefore; Tanjero Formation is widespread in Balambo-Tanjero, High Folded, and some parts of Low Folded Zone. Toward the SW direction, Hadiena, Aqra, and Bekhma formations which were deposited in shallow environments; which in turn, pass laterally into basinal marl and carbonate of Shiranish Formation deposited.

Material and Methods

Seventeen (17) rock samples (15 from Dokan and 2 from Shaqlawa) of Tanjero Formation were collected from Dokan and Shaqlawa areas (Figure 1). All samples were washed with water and dried. The Total Organic Carbon (TOC) content was measured for all samples using LECO instrument. According to Tissot and Welte, (1984), rocks that have TOC values more than 0.5 wt. % are considered potential source rocks.

50-120 mg of powdered sample was used for Rock-Eval Pyrolysis analysis. In this analysis, the sample is heated to 300°C using helium as carrier gas; this temperature will vaporizes the already present bitumen (S1) peak. The temperature is then raised progressively to 600°C at a rate of 25°C/min. converting all the remaining petroleum potential of the kerogen into bitumen and gas (S2). CO_2 expelled from the organic matter also measured as S3. The temperature of peak hydrocarbon generation due to thermal cracking of kerogen, that is, the temperature with the peak of S2 is called Tmax.

The samples with higher TOC vales were chosen for bitumen extraction. Bitumen was extracted from 3 to 5 g of powdered y using dichloromethane (DCM) as a solvent. The mixture of sample and solvent was mixed by a magnetic stirrer for 24 hr. The extracts was filtered and concentrated in an evaporator. The deasphalted extract fractionated into three fractions (saturated hydrocarbons, aromatic hydrocarbons, and resin) by column chromatography on silica gel. The saturated hydrocarbons were analyzed by Fisons Instruments GC 8000 series ECD 850 Gas Chromatography–Flame Ionization Detector (GC-FID). Hydrogen was used as carrier gas. The program of the oven temperature was 80°C for 5 min to 300°C for 20 min at 5°C/min.

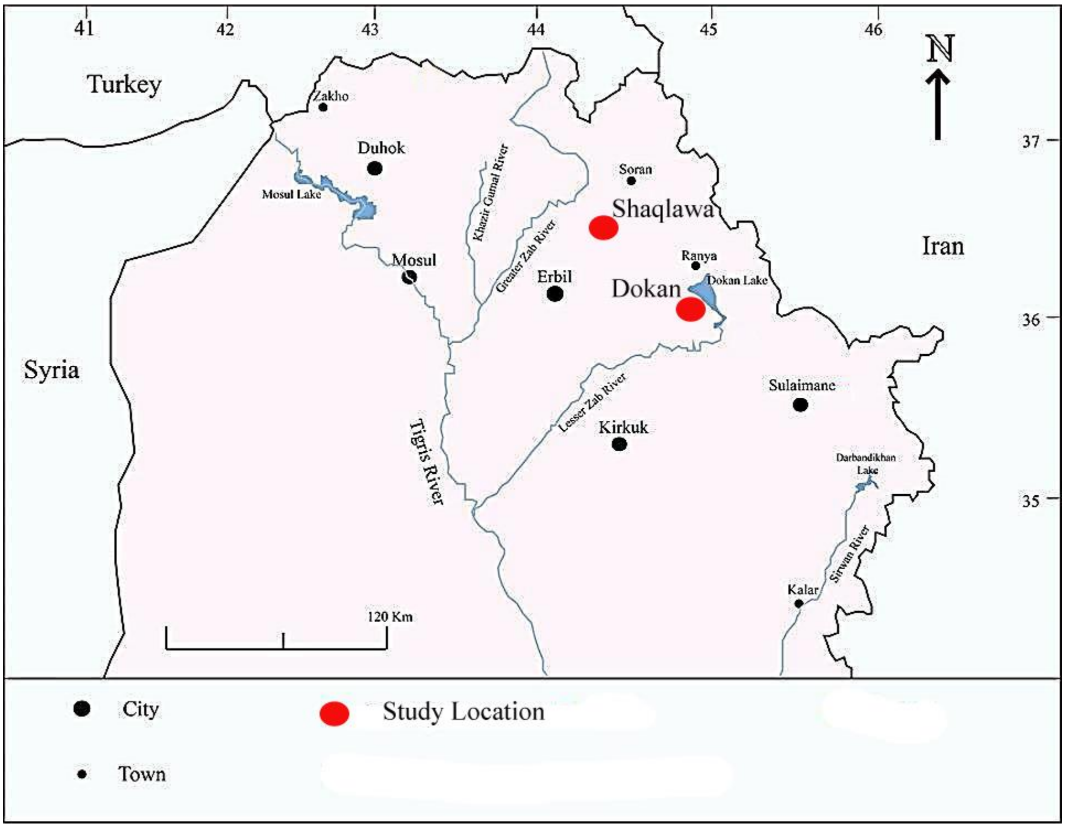

Figure (1): Map of north Iraq showing the locations of the study areas

Results and Discussion

Total Organic Carbon (TOC) values and Rock-Eval pyrolysis results are shown in table 1. TOC values are generally low; they are between 0.07 and 0.21 wt. % in Dokan (except for one sample with higher value 0.54) and 0.43-0.45 wt% in Shaqlawa. According to Peters, 1986 and Peters and Cassa, 1994; Tanjero Formation at Dokan and Shaqlawa can't be considered as potential hydrocarbon source rocks.

Table 1. TOC, carbonate content, Rock-Eval pyrolysis, Pr/Ph and EOM results of the studied samples

Samples	Location	Carbonate Content (wt%)	TOC (wt%)	S1	S2	S3	Tmax (°C)	(HI)	(OI)	Pr/Ph	EOM (ppm)
1	Dokan	34.49	0.54	0.05	0.53	1.17	425	98	216	1.68	293
2	Dokan	48.92	0.14	0.04	0.05	0.25	452	35	177	-	-
3	Dokan	27.43	0.14	0.03	0.04	0.25	437	29	184	-	-
4	Dokan	47.81	0.21	0.03	0.10	0.23	437	47	108	1.86	218
5	Dokan	56.19	0.10	0.03	0.02	0.38	445	21	394	-	-
6	Dokan	24.45	0.12	0.03	0.04	0.22	434	34	186	-	-
7	Dokan	25.91	0.09	0.03	0.03	0.25	420	35	288	-	-
8	Dokan	21.63	0.07	0.05	0.03	0.23	428	42	325	-	-
9	Dokan	24.29	0.14	0.04	0.04	0.12	440	28	83	-	-
10	Dokan	71.90	0.21	0.02	0.03	0.42	442	14	199	-	-
11	Dokan	23.22	0.14	0.04	0.05	0.21	431	36	152	-	-
12	Dokan	22.40	0.20	0.03	0.04	0.31	429	20	157	1.79	184
13	Dokan	58.58	0.13	0.05	0.08	0.27	425	61	206	-	-
14	Dokan	27.48	0.08	0.06	0.01	0.32	431	13	404	-	-
15	Dokan	55.12	0.11	0.03	0.05	0.38	436	44	336	-	-
16	Shaqlawa	34.02	0.43	0.04	0.19	0.19	430	44	44	-	-
17	Shaqlawa	41.44	0.45	0.05	0.09	0.26	437	20	57	-	-

S1 and S2 in (mg HC/g); S3 (mg CO2/g); HI= Hydrogen Index (S2x100/TOC); OI= Oxygen Index ((S3x100/TOC); EOM= Extractable Organic Matter

There are many reasons for low TOC values of Tanjero Formation at Dokan and Shaqlawa. First, the dilution effect when the basin came under the influence of a stronger clastic input and high sedimentation rate with the formation of organic- lean sediments. Second, these organic- lean sediments could have been deposited under more oxic environment. Third, weathering (oxidation) effect when ancient organic matter exposed directly to atmospheric conditions, they subjected to weathering effects. Climate, source and maturity of organic matter are the main factors controlling the weathering rate of the ancient organic matter (Marynowsyi et al., 2011). Weathering, especially oxidation, will change the original composition of the organic matter on bulk and molecular levels. The major changes are represented by decrease the TOC, extractable organic matter (EOM), and concentration of individual compounds (Marynowski and Wyszomirski, 2008; Marynowsyi et al., 2011). As we stated above, the TOC values decrease upward from 0.54% near the contact with Shiranish Formation, to less than 0.1% in the upper part of Tanjero Formation. In addition, extractable organic matter (EOM) decrease from 293 ppm in sample 1, 218 ppm in sample 4, to 148 ppm in sample 12. Moreover, subsurface samples of Tanjero Formation in Bijeel-1 Well (60 km north of Erbil) have higher TOC values (0.99-1.08 wt. %)(Abdula et al., 2017). These criteria suggest that organic matter of Tanjero Formation at Dokan area could be subjected to weathering (oxidation) effect which led, in participation with high sedimentation rate and low productivity, to reduce the TOC values.

Type of Organic Matter:

Rock-Eval pyrolysis parameters are widely used to recognize organic matter type. The elevated oxygen index (OI) (44- 404; average 206) and low hydrogen index (HI) values (14-98; average 37) of all samples indicate presence of type IV and III kerogen, composed mainly of terrestrial organic matter, or reworked and oxidized organic matter (Tissot and Welte, 1984; Peters et al., 2005). This assumption is supported by TOC-S2, HI-Tmax and HI-OI diagrams (Figure 2). The presence of type III and IV kerogen in these two locations indicate presence of inert organic matter that affected by high level of thermal maturity or weathering (oxidation). The maturity effect can be excluded where Tmax vlaues of most samples are generally low (less than 440 ^{o}C); therefore, oxidation effect suggested to be responsible for the presence of type IV kerogen.

Gas chromatography (GC) chromatograms of two samples (1 and 12) show unimodal distributions of normal alkanes with short- chain predominance maximum at C15-C18, with harmonic decrease of normal alkanes abundance with increasing carbon number (Figure 3). Third sample (sample 4) show biomodal distributions of normal alkanes with two humps. The first hump at C15 and C16, and the second at C31. This distribution typical of mixed marine and terrigenous organic matter (Tissot and welte, 1984; Killos and Killos, 2005; Peters et al., 2005). Abundant short chains of normal alkanes (particularly C17) indicate algal contribution to the organic matter (Tissot and Welte, 1984; Hunt et al., 1996); whereas normal alkanes with odd-carbon number; particularly C27, C29, and C31; indicate significant contribution of higher plants (Tissot and Welte, 1984; Peters et al., 2005). The high contribution of marine (algal) organic matter in Tanjero Formation is inconsistent with kerogen type inferred based on rock-eval pyrolysis parameters (discussed above) which suggest high contribution of terrestrial organic matter. However, this inconsistency could be due oxidation effect which led to short chain (C17-C19) predominance over long chain (C27-C33) normal alkanes. The short chain predominance in oxidized ancient organic matter is also previously reported by observed Marynowski and Wyszomirski, (2008). These authors observed that there are long chain degradation which led to gradual increase in short chain abundance. The presence of terrestrial organic matter is expected where clastic sediments of Tanjero Formation were generated from ophiolite sheet erosion and they were deposited in marine environment.

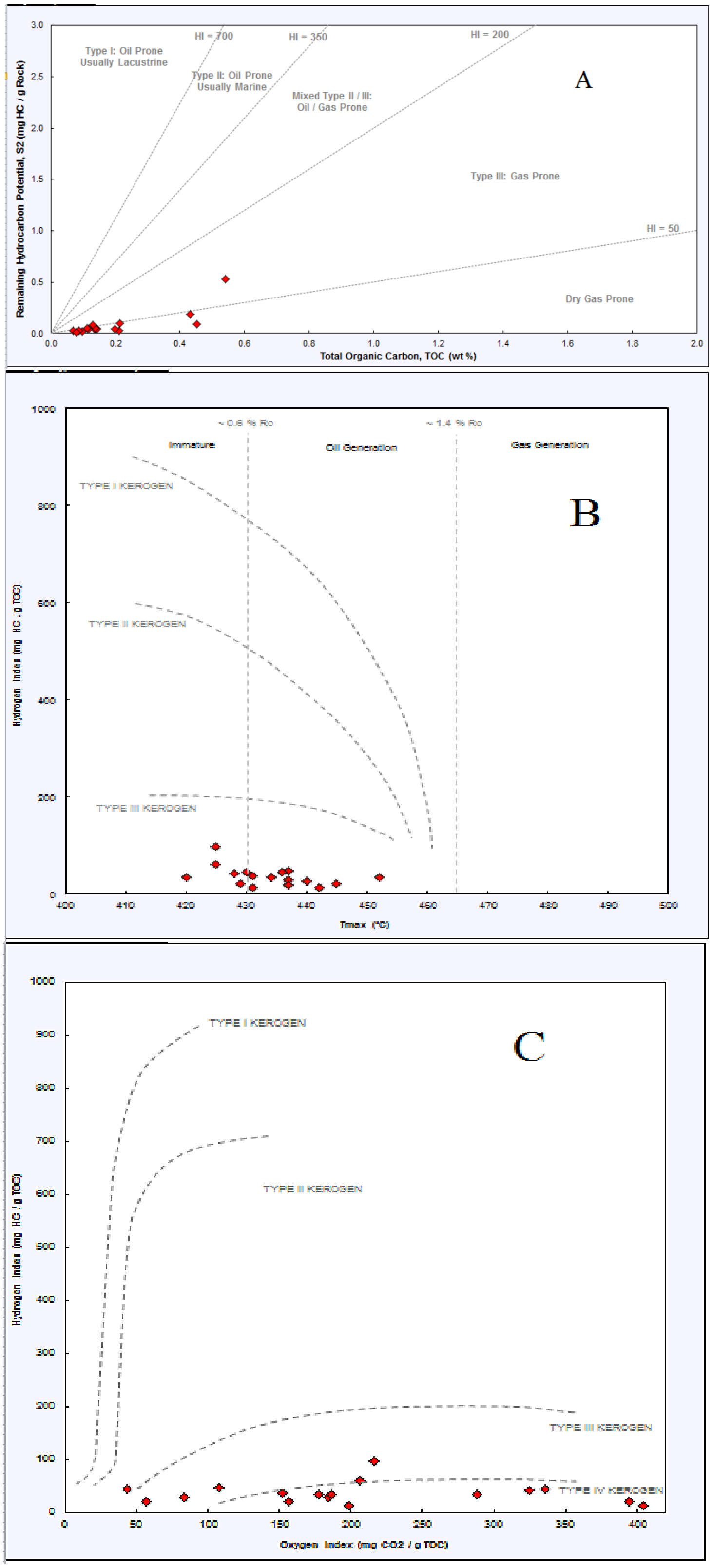

Figure 2: Organic matter type of Tanjero Formation based on (A): TOC-S2 relationship; (B): HI-Tmax relationship; and HI-OI relationship.

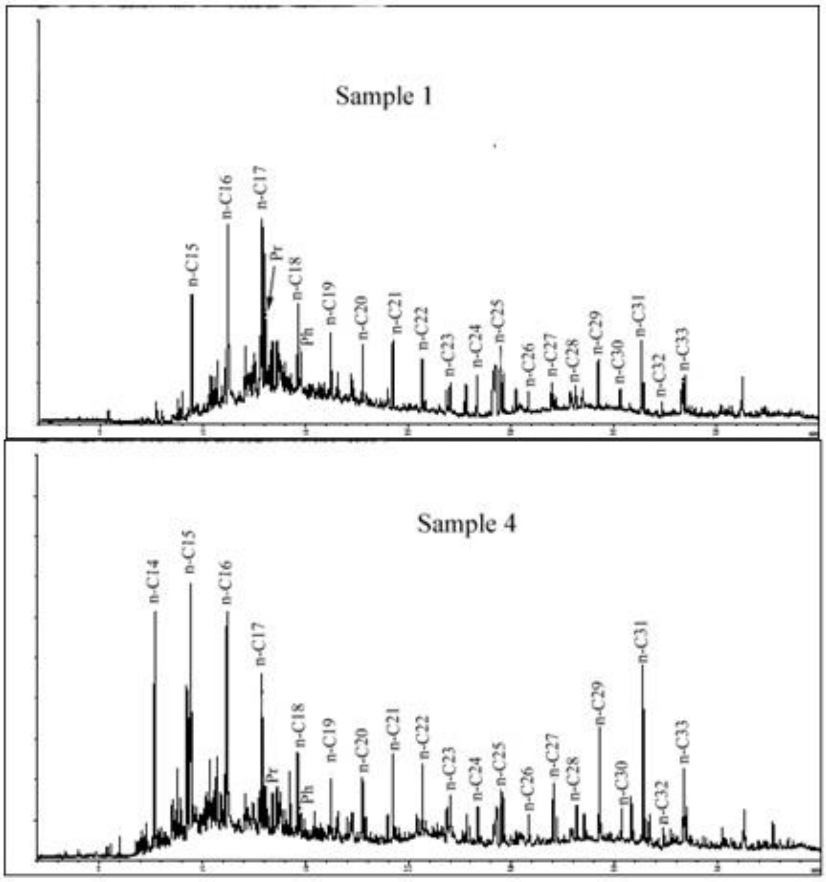

Figure 3. GC-FID chromatograms of saturated hydrocarbons of two samples.

Depositional environment

Carbonate Content (CC) of the studied samples of Tanjero Formation is variable between 21.6-71.9 wt.% and 34.0-41.4 wt.% in Dokan and Shaqlawa, respectively. The high CC of some samples suggests strong marine or lacustrine influence (Sachse et al., 2011); whereas the low- medium CC of other samples suggest marine depositional environment with high influence of terrestrial input. The low TOC and CC values of Tanjero Formation suggest oxic depositional environment. In addition, the high pristane/phytane ratio of Tanjero Formation (1.68-1.86; Table 1) is strong indication for deposition under oxic environment (Didyk et al., 1978; Peters et al., 2005).

The weak relationship between TOC and CC (Figure 4) could indicate that marine organic matter input is constant (and low) while terrigenous organic matter input is variable, or the total organic matter input is constant whereas the dilution effect (carbonate and clastics) is variable. (Jassim and Buday, 2006a) mentioned that Tanjero Formation become more thinly bedded and fine grained southwestward. This observation associated with higher TOC values (as in Shaqlawa and Bijeel) indicate that depositional environment of Tanjero Formation is less affected by clastic input toward southwest; and may indicate that Tanjero Formation may have source rock characteristics in Low Folded Zone.

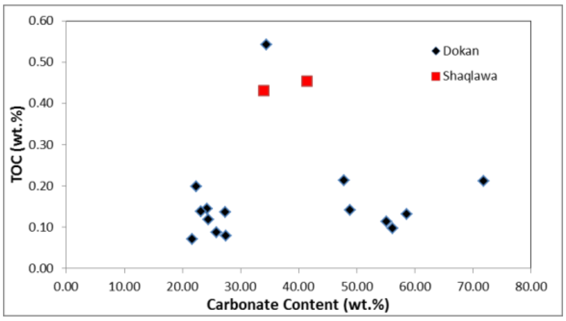

Figure 4: TOC-Carbonate relationship of Tanjero Formation

Conclusions

The main conclusions of this study are:

1. Tanjero Formation at Dokan and Shaqlawa areas have low TOC values; therefore; they cannot be considered as potential source rocks.
2. Organic matter of Tanjero Formation at Dokan and Shaqlawa are of terrestrial origin and they are affected by weathering (oxidation) which led to reduce TOC values and for presence of type IV kerogen.
3. Low TOC and high Pr/Ph values indicate that Tanjero Formation at these two localities was deposited under oxic depositional environment

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الجيوكيمياء العضوية لتكون تانجيرو في مناطق دوكان وشقلاوة شمال العراق: دلائل الترسيب في بيئة مؤكسدة

محمد وكاع عجيل الخفاجي ، سلام ابراهيم محمود الجبوري

الملخص

تمت دراسة صخور تكوين تانجيرو في مناطق دوكان وشقلاوة لتحديد مدى قابليتها لتوليد الهيدروكاربونات وتحديد ظروف بيئة الترسيب. ولهذا الغرض فقد تم قياس محتوى الكاربون العضوي والتحليل بتقنية التكسر الحراري لـ 17 نموذجا من صخور التكوين. كما تم استخلاص المواد العضوية القابلة للاستخلاص (البتيومين) وفحصه بتقنية كروماتوغرافيا الغاز لثلاثة نماذج.

بشكل عام فان قيم محتوى الكاربون العضوي و S2 لصخور تكوين تانجيرو كانت قليلة (0.07-0.54%) و 0.01-0.53 على التوالي) والتي تدل على ان صخور التكوين ذات قابلية منخفضة لتوليد الهيدروكاربونات. اظهرت معاملات التكسر الحراري (معامل الهيدروجين ومعامل الاوكسجين و Tmax) ان المواد العضوية في صخور تكوين تانجيرو هي من النوع الثالث والرابع. اما نتائج تحليل كروماتوغرافيا الغاز فيدل على ان صخور التكوين قد ترسبت في بيئة مؤكسدة. ان تاثير التجوية، وخصوصا الاكسدة، ادى الى نقصان محتوى الكاربون العضوي والبتيومين في صخور تكوين تانجيرو قيد الدراسة.