Qatar Univ. Sci. J. (1994), 14 (2): 368-372

# LOWER EOCENE BLACK SHALE BEDS OF RUS FORMATION IN NORTH OF OMAN-POSSIBLE OIL SHALES

By

S. AL-HAJARI and K. A. KHALED
Department of Geology, Faculty of Science, University of Qatar, Doha, Qatar

# طبقات صخور الطفلة السـوداء لعصر الأيوسين في تكوين «رس» بشمال سلطنة عمان ـ إحتمال كونها صخور طفلة زيتية

سيف علي الحجري و خالـد أحمـد خـالد

تمت دراسة مجموعة من عينات صخور الطفلة السوداء المأخوة من تكوين «رس» في شمال سلطنة عمان . وقد أوضحت نتائج الدراسة أن هذه الصخور تحتوي على نسبة عالية من المواد العضوية حيث تصل نسبة المواد البيتومينية بها إلى ٨,٥٪ ونسبة الكربون العضوي إلى ١٢,١٧٪ بينما تبلغ نسبة ما تحتويه من كيروجين حوالي ٢١,٢٧٪ ، كما أن هذه الصخور تعطي عند تحليلها بطريقة فيشر حوالي ٢٠ جالون أمريكي من زيت البترول لكل طن .

وأثبتت الدراسة أن صخور الطفلة تحتوي على كيروجين غني بالهيدروجين ويتبع النوع الأول والثاني غير الناضج .

وخلصت الدراسة إلى أن طبقات الطفلة السوداء بالمنطقة تعتبر صخور طفلة زيتية غنية بالمواد العضوية ولها جهد عال لإنتاج المواد الهيدروكربونية .

*Key Words*: Black Shales, Rus Formation, Oil Shales, Oman

## ABSTRACT

A suite of samples from some black shale beds of lower Eocene Rus Formation from north of Oman have been investigated through detailed geochemical analyses. The obtained results indicate that these shale beds contain a significant amount of either soluble or insoluble organic matter. The total extractable dissolved organic matter content ranges from 3.5% to 5.8%, and Fischer Assay yields up to 20 U.S. gal/ton of oil. The average value of the total organic carbon content for these rocks is about 17.12% and that of kerogen content equals 27.21%.

The elemental analysis, vitrinite reflectances, IR-spectra, and TGA and DTG curves of kerogen isolates indicate that studied shales contain Types I and II kerogen which attained only an immature thermal maturation stage. The study reveals that Rus Formation black shale beds appear to have a good potential for shale oil production in north of Sultanate of Oman.

## INTRODUCTION

The Tertiary sedimentary rock sequence in the northern region of Oman contains many shale beds. The study reported in this paper deals with the organic geochemical characteristics of some black shale beds which interbedded in Rus Formation and attention is focused on the kerogen isolates. The studied area lies about 50 kms WSW of Muscat the capital of Sultanate of Oman (Fig. 1). The examined shale samples had been taken from outcrops along the Seeb - Al Khod road, particularly those at the road - cut which lies about one kilometer NE of Al Khod village (Fig. 2). The surface section of Tertiary rocks in this area consists of three formation named from base to top as follows: Umm er Radhuma (Jafnayn), Rus (Rusayl), and Dammam or Seeb Formation (Fig. 3).

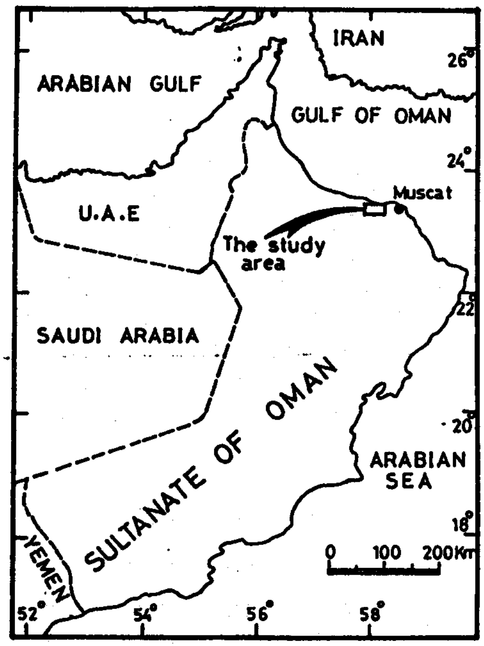


Fig. 1: Location map of the studied area.

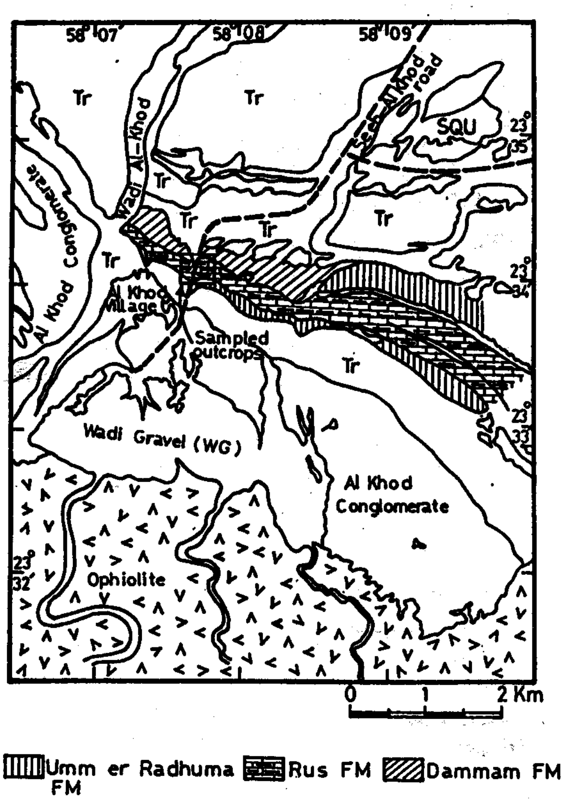


Fig. 2: Geological map of Al-Khod area

Thirty fresh samples were collected from black shale beds in Rus Formation of lower Eocene age. This formation is developed in an evaporitic facies consisting of steeply dipping gypsum and anhydrite beds associated with variable dolomite and dolomitic and/or marls interbedded with orange, brown, and black colored shale beds. Based on the previous published works, Rus Formation is barren of fossils and probably is deposited in a restricted lagoons, playa or sabkha setting. It has a wide spread occurrence indicating a regional sea-level fall from a stable shelf [1, 2]. The total thickness of Rus Formation in the area reaches about 200 m including the shale beds of thickness ranges from 1 to 3 m for each.

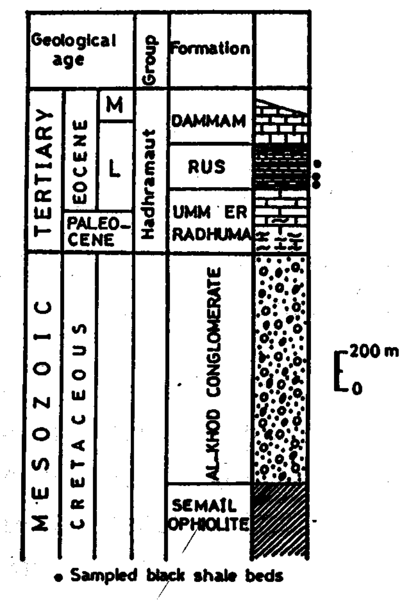


Fig. 3: Chrono- and lithostratigraphic subdivisions of Tertiary sedimentary sequence in the studied area.

In general, Tertiary rocks in the area were subjected to folding forces which gave rise to a harmonic style of folds. Consequently, a several plunging anticlines and synclines are obviously observed in Rus Formation rocks in the studied area.

## EXPERIMENTAL

Shale samples were crushed to give particles of size 200 mesh. Each powdered sample of around 100 gm was subjected to successive extraction process by Soxhlet with redistilled chloroform and a mixture of ethanol - benzene. The total extractable dissolved organic matter (EOM) was determined and standard Fischer Assay was carried out for each sample. Kerogens were isolated from 15 selected samples using a procedure modified from Saxby [3] and Brass and Williams [9]. The total organic carbon content (TOC) of the given rock powder (after decarbonation by 10% Hcl) and the elemental analysis (C, H, N) of kerogen isolates were determined using Leco CHN 600 instrument. In addition, TGA was carried out for kerogens using Perkin - Elmer TGA-7 instrument under nitrogen atmosphere and temperature program from 25°C to 800°C and heating rate of 4 C/min. IR spectra of kerogen samples were also obtained using Nicolet 510 p FT - IR spectrometer and KBr powder for preparing sample pellets. The vitrinite reflectance were measured using the light reflectance measurements at 546 nm in oil (n=1.518 at 24°C).

The above mentioned analyses had been carried out in different laboratories in Faculty of Science and Scientific

Research Centre (S.A.R.C.) in the University of Qatar (Qatar), and Faculty of Petroleum and Mining Engineering in Suez Canal University (Egypt). In addition, some analysis were carried out abroad in the University of Southampton (U.K.)

## RESULTS AND DISCUSSION

The studied samples represent shale beds of black to dark gray color having a marked and easily detectable bitumen odour. The obtained analytical results are summarised in Table 1 showing that these shales consist mainly of clay grains as indicated by the silicate content value which ranges from 33.08% to 36.82%, and calcium carbonate content value which lies between 30.78% and 32.9%. Therefore, these rocks could be also considered as limy shales or marls.

**Table 1**
Geochemical analysis of lower Eocene Rus Formation black shales, north of Oman

| No. | Silicates % | Carbonates % | EOM % | TOC % | Kerogen % |
|---|---|---|---|---|---|
| 1 | 34.71 | 30.88 | 58413 | 17.25 | 27.61 |
| 2 | 35.66 | 31.50 | 41692 | 17.23 | 27.30 |
| 3 | 33.08 | 32.90 | 43200 | 17.10 | 27.20 |
| 4 | 36.40 | 32.12 | 38405 | 17.22 | 27.50 |
| 5 | 35.29 | 32.56 | 39987 | 16.98 | 26.80 |
| 6 | 33.18 | 32.13 | 50781 | 17.00 | 27.10 |
| 7 | 36.49 | 31.41 | 35362 | 17.24 | 27.35 |
| 8 | 34.88 | 32.07 | 42125 | 16.99 | 26.85 |
| 9 | 36.69 | 31.79 | 37997 | 16.97 | 26.79 |
| 10 | 33.44 | 32.65 | 45711 | 17.11 | 27.30 |
| 11 | 36.42 | 31.98 | 36212 | 17.21 | 27.25 |
| 12 | 35.43 | 32.66 | 40822 | 17.16 | 27.28 |
| 13 | 34.71 | 32.49 | 43542 | 16.96 | 27.10 |
| 14 | 36.79 | 31.17 | 38264 | 17.22 | 27.40 |
| 15 | 36.82 | 30.78 | 35008 | 17.20 | 27.30 |

The EOM value of samples ranges from 35008 ppm to 58413 ppm with average value equals 41834 ppm. The average value of Fischer Assay oil yields of the samples measures about 20 U.S. gal/ton (5.84 wt. %) of oil. The minimum value of TOC of samples is 16.96%, while the maximum one is 17.25% and the average value amounts 17.12%. This is considered as a high organic carbon content in comparison with TOC values of some other known oil shales in the world such as: Crevenay Severac in France (5-10%), Scotland oil shales (12%), Eastern Desert oil shales of Egypt (up to 13%), Green River shale in Colorado U.S.A. (11-16%), Nova Scotia oil shales in Canada (8-26%, Glen Davis oil shales of Australia (40%), and oil shales of Estonia (77%), Tissot and Welte, [5]. This high TOC of the studied shales is proved also by the measured kerogen content which its value lies between 26.79% and 27.61% giving an average value of about 27.21%. In general, the obtained results indicate that Rus Formation black shale beds in north of Oman are organic-rich rocks.

The separated kerogens have been classified according to the classification of Tissot *et al.,* [6] using the elemental analysis of three elements C, H, and O. Based on the H/C and O/C atomic ratios kerogen types of the studied samples are determined using the van Krevelen's diagram in Fig. 4. This Figure shows that kerogens under investigation are characterised by a high hydrogen content as their H/C atomic ratio ranges from 1.37 to 1.5, and low oxygen content indicated by O/C atomic ratio which lies between 0.1 and 0.14 (Table 2). According to these values the kerogen isolates are located within the diagenesis stage of maturation of types I and II kerogens. This indicates that the studied shales contain an immature organic matter of Types 1 and II kerogen which have a good hydrocarbon generating potential for oil and gas as denoted by Tissot and Welte [7] and Bailey [8]. This is could also proved by the vitrinite reflectances (R, %) of these samples which always measure an value less than 0.5% and thermal alteration index (TAI) ranges from 2 to 2.3 (Table 2).

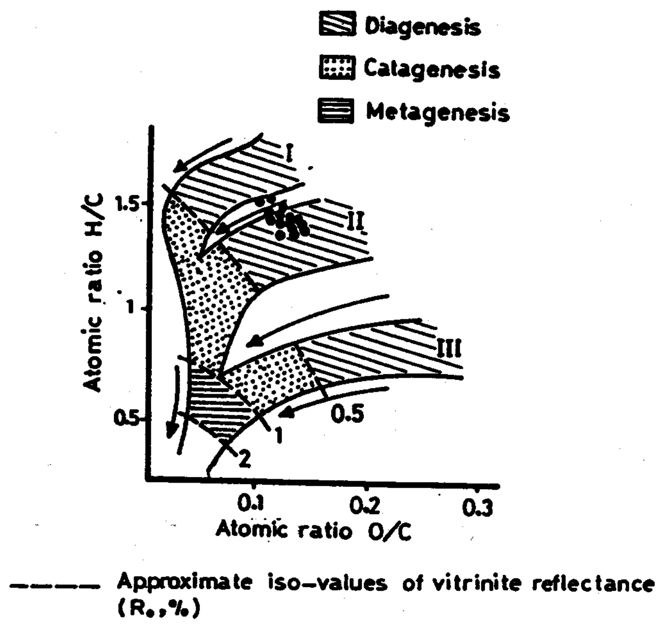


Fig. 4: The elemental composition and types of kerogen of the Rus Formation black shales (North of Oman)

The shape of the obtained TGA and the time derivative of the thermogravimetry curve "DTG" of sample No. 1 are shown in Fig. 5. Three stages are recognized in the TGA curve. The first stage continues up to about 200 C involving a rather small loss of weight which measures about 5%; the second one lies between 200 C and 300 C reflecting an important loss of weight (80%); while the third stage is located above 300 C showing a small loss of weight also (12%). These curves also show that the maximum rate of weight loss lies at 250 C (on the DTG curve) and the total weight loss amounts about 92.5% (on the TGA curve) which characterises the diagenesis stage of maturation and a low maturity level of the studied samples [7, 9 and 10].

**Table 2**
Elemental analysis and vitrinite reflectances of kerogen isola
Rus Formation black shales

| No. | Elemental | | Analysis | | Atomic Ratios | | R, % | TAI |
|---|---|---|---|---|---|---|---|---|
| | C | H | O | S | H/C | O/C | | |
| 1 | 76.10 | 9.51 | 10.15 | 3.75 | 1.50 | 0.10 | 0.4 | 2.3 |
| 2 | 75.90 | 9.36 | 12.14 | 1.80 | 1.48 | 0.12 | - | - |
| 3 | 75.53 | 8.81 | 13.09 | 1.95 | 1.40 | 0.13 | - | - |
| 4 | 75.81 | 9.29 | 11.12 | 2.88 | 1.47 | 0.11 | 0.4 | 2.3 |
| 5 | 75.45 | 8.68 | 13.08 | 1.79 | 1.38 | 0.13 | - | - |
| 6 | 75.71 | 8.83 | 14.13 | 0.85 | 1.40 | 0.14 | - | - |
| 7 | 76.00 | 9.18 | 13.17 | 0.93 | 1.45 | 0.13 | 0.3 | 2.0 |
| 8 | 75.50 | 8.75 | 13.09 | 1.86 | 1.39 | 0.13 | - | - |
| 9 | 75.40 | 8.67 | 14.07 | 0.98 | 1.38 | 0.14 | - | - |
| 10 | 75.86 | 9.10 | 12.14 | 2.10 | 1.44 | 0.12 | - | - |
| 11 | 75.93 | 9.24 | 11.14 | 2.89 | 1.46 | 0.11 | 0.4 | 2.3 |
| 12 | 75.85 | 8.91 | 13.15 | 1.39 | 1.41 | 0.13 | - | - |
| 13 | 75.78 | 8.65 | 12.13 | 2.64 | 1.37 | 0.12 | - | - |
| 14 | 75.95 | 9.43 | 11.14 | 2.78 | 1.49 | 0.11 | 0.4 | 2.3 |
| 15 | 75.91 | 9.17 | 12.15 | 1.97 | 1.45 | 0.12 | 0.3 | 2.0 |

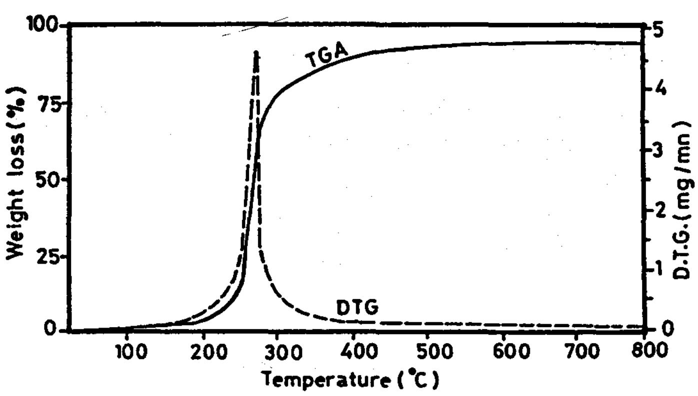


Fig. 5: The TGA thermograms of Kerogen concentrate of Rus Formation black shales (sample No. 1), North of Oman.

The IR spectrum o the same sample (No. 1) shows marked bands in Fig. 6. This spectrum presents a medium bank characterises kerogen of a relatively high hydrogen content. This band is produced due to the skeletal vibration of straight chains with more than four CH groups [11]. The band at 1400 - 1450 cm-1 is due to asymmetric 1370 cm-1 is mainly due to asymmetric bending of the CH3 group only. The strong and wide peaks at 1630 - 1660 cm-1 range mostly are attributed to aromatic C=C with contribution of olefinic C=C, C=O groups of the carbonyl group and to the free water [12]. The strong peaks located at 2855 and 2922 cm-1 are mainly due to the asymmetric and symmetric stretching of alkyl CH2 and CH3 aliphatic groups. At this range the band shows no broading which sometimes appears as a shoulder at 2900 cm in spectra of coal and kerogens of very low hydrogen content and high CH3 content such as kerogen of Type III [13]. The broad band located at 3250 - 3450 cm-1 region is carboxylic groups. Extension of this band towards the low wave-numbers (below 3000 cm-1) reflects the presence of strong hydrogen bonding of carboxylic acids. The stretching of this band could be also attributed to the high molecular water content (moisture) held by kerogen macerals [12 & 14]. However the obtained IR spectra of the studied kerogen samples are generally similar indicating kerogen to be immature and mainly aliphatic.

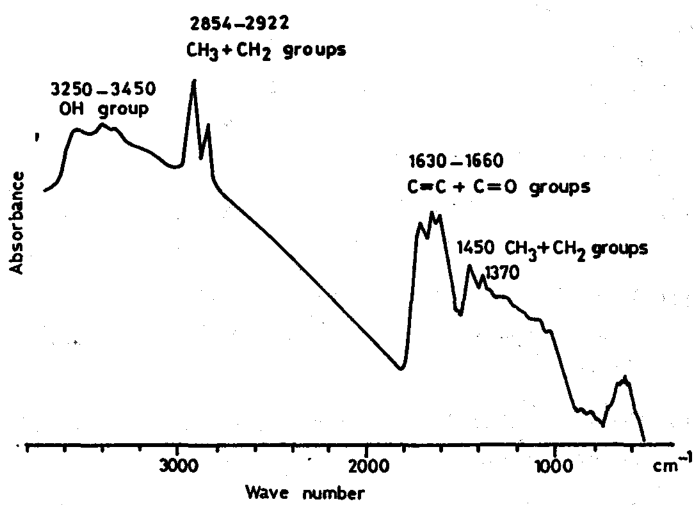


Fig. 6: IR spectrum of kerogen concentrate of Rus Formation black shales (sample No. 1), North of Oman.

The aforementioned results and discussion indicate that Rus Formation black shales beds in north of Sultanate of Oman appear to have a good potential for shale oil production. Therefore, it is considered here as to be oil shale rocks. In addition, based on the mineralogy (high carbonate content), the associated sediments (saline minerals), and the obtained organic geochemical characteristics these oil shale beds seems to be deposited in an environment of large lake basins or lagoons according to Duncan review [15] of the different main geologic environment in which oil shales are deposited.

## CONCLUSIONS

The lower Eocene Rus Formation shale beds in north of Sultanate of Oman are considered as to be organic-rich oil shales as their TOC value is generally in the 16.96% to 17.25% range and Fischer Assay oil yields up to 20 U.S. gal/ton. The organic matter of the studied samples consists of kerogen of Types I and II having a high contents of hydrogen and aliphatic compounds, and has reached only an immature thermal maturation level (diagenesis stage). These oil shale beds seem to be deposited in large lake basins and lagoons. It is concluded also that the studied shales could act as a source rock having a good potential for shale oil production.

## ACKNOWLEDGEMENTS

The authors would like to express their gratitude to the Authorities of the Faculty of Science and S.A.R.C. in the University of Qatar (Qatar) and Faculty of Petroleum and Mining Engineering in Suez Canal University (Egypt) for help to the analytical program of this study. Appreciating is also due to Dr. S. Hanna (Associate Professor SQU, Oman) for providing of field data and his support of the investigation in Oman. Special thanks is also due to Dr. Marshall J.E.A. (University of Southampton, UK) and A. Ali Akbar (Associate

Lecturer, Geology Department, Qatar University) for his help to the analytical course abroad.

## REFERENCES

[1] **Powers, R.W., 1968.** Lexique stratigraphique International: 3, Asie. Fasc. 10b 1 Arabia Saoudite), Paris.

[2] **Cavelier, C., 1970.** Geological description of the Qatar peninsula (Arabian Gulf). Government of Qatar, Department of Petroleum Affairs. Bureau de recherches geologiques et minieres, Paris, France.

[3] **Saxby, J.D., 1970.** Technique for isolation of kerogen from sulfide ores. Geochim. Cosmochim. Acta, 34: 1317-1326.

[4] **Brass, M.C.** and **G.L. Williams, 1973.** Palynology and nanofossils processing techniques, Geol. Surv. Canada. 73-76, 1-25.

[5] **Tissot, B.** and **D.H. Welte, 1984.** Petroleum formation and occurrence. 2nd ed. Springer, New York.

[6] **Tissot, B., B. Durand, J. Espitalie** and **A. Compaz, 1974.** Influence of the nature and diagenesis of the organic matter in formation of petroleum. Bull AAPG. 58: 499-506.

[7] **Tissot, B.** and **J. Espitalie, 1975.** L Evolution thermique de la matiere organique des sediments: Application d une simulation mathematique, Inst. France Petr. Rev., 30: 743-777.

[8] **Bailley, N.J.I., 1983.** Hydrocarbon potential of organic matter. In: Brooks, J. (ed.). Organic maturation studies and fossil fuel exploration, Academic Press. London 283-302.

[9] **Durand, B., J. Espitalie, G. Nicaise** and **A. Compaz, 1972.** Etude de la matiere organique insolubel (Kerogene) des argiles du Toarcian Du Bassin de Paris. I, Etude par les procedes optiques, analyse elementaire, etude en microscopie et diffraction electroniques, Rev. Ins. Fr. Petr., 27: 865-884.

[10] **Durand, C.** and **Souron, 1980.** Thermogravimetric analysis and associated techniques applied to kerogens. In: Kerogen insoluble organic matter from sedimentary rocks. Edited by Durand, B., Editions Technip, Paris, France.

[11] **Bellamy, L.F., 1975.** The infrared spectra of complex molecules. 3rd., ed., Chapman and Hall.

[12] **Robin. P.L.** and **P.G. Rouxhet, 1976.** Contribution des differences fonctions chimiques dans les bands du adsorption infrarouge des kerogenes situees a 1710, 1630 et 3439 cm-1, Rev. Inst. France Petr. 31: 955-977.

[13] **Robin, P.L., P.G. Rouxhet** and **B. Durand, 1977.** Characterization des kerogenes et de leur evolution par spectroscopie infrarouge. In: Advances in Organic Geochemistry, 1975. Campos, R. Goni, J. (eds.) Madrid, 693-716.

[14] **Schafer, H.N.S., 1972.** Fuel, 51, 4.

[15] **Duncan, D.C., 1967.** Geologic setting of oil shale deposits and world prospects. Proc. 7th World Petro. Cong. 3, 659-667.