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Thesis Changes Log

Name of Candidate: Timur Bulatov

PhD Program: Petroleum Engineering

Title of Thesis: The lithological and geochemical study of Type I kerogen in the Bazhenov Formation in application to exploration and production of hydrocarbons

Supervisor: Prof. Mikhail Spasennykh

Co-supervisor: Dr. Elena Kozlova

The thesis document includes the following changes in answer to the external review process.

Dear Jury Members,

I would like to express my gratitude for your comments and suggestions to all of you! I found them very useful and it helped to significantly improve my PhD thesis.

Sincerely,
Timur Bulatov

Reviewer: Professor Ksenija Stojanović

1. *Abstract, fifth line from the top: The sentence "The majority of petroleum source rocks for oil fields." should be deleted.*

   Response: Thank you! Done.

2. *Title of sub-chapter 2.1.: Replace source by sources.*

   Response: Corrected.

3. *Page 56, fourth line from the top: Replace oh by of.*

   Response: Done! Thanks for the correction!

4. *Page 72, the second paragraph: The last sentence in this paragraph "The carbon isotope composition for the alginite-rich layers varies in the range from −31.1 to −31.9‰, while for the host rocks $\delta^{13}C_{org}$ it varies from −30.5 to −31.9‰." should be deleted since it represents repetition of the previous sentence.*

   Response: Thank you! Done.

Reviewer: Professor Naima Hamoumi

1. *It's more appropriate to replace "lithological methods with "Sedimentological methods" in all the manuscript (abstract, Introduction, chapter 3 etc.…), because the techniques used are: Thin section petrography, Organic petrography, Scanning electron microscopy, and X-Ray diffraction.*

Response: Dear prof. Naima Hamoumi, thank you for your valuable comment. Probably, in the case of emphasis on sedimentation environments, it would be worth changing the term. But we put in the meaning of "lithological" also secondary changes in catagenesis. Therefore, it is important for us to emphasize that this is no longer sediment, but *lithos* – a stone.

2. *It would be useful to add in Chapter 2 a bibliographical synthesis on the geological and geodynamic context of the Upper Jurassic – Lower Cretaceous Bazhenov Formation and the West Siberian Petroleum Basin. Such compilation may help to validate and support the proposed interpretations.*

Response: Thank you for the suggestion! In Chapter 2 I put information only about world-known deposits containing type I kerogen. But I put more information about the Upper Jurassic – Lower Cretaceous Bazhenov Formation and the West Siberian Petroleum Basin in 1.1 General overview (Page 17-18).

3. *"Accepted classifications" (3.3, L.3, Pages. 43 and 44) "Accepted classifications should be replaced with "Adopted stratigraphic subdivisions and classification"*
   3.3.1 Tectonic units
   3.3.2 ~~3.3.3 Stratification~~ Stratigraphy of the Bazhenov sequence
   3.3.3 ~~3.3.2~~ Thermal maturity of organic matter

Response: Thank you! Done.

4. *What do you mean by "facial settings"? (L 2 of the summary of chapter 2)*

Response: Here, I mean depositional environments. I removed "facial settings" and put "depositional environments".

5. *According to Figure 4.1.1. in Page 45, it seems that you have at least 4 different sedimentary facies. It would be useful to conduct a sedimentary facies analysis of the core. The study of sedimentary facies is of great value for oil exploration. In addition to recognition and palaeogeographic reconstruction of sedimentary environments, it helps to better analyze the reservoir characteristics.*

Response: Dear prof. Naima Hamoumi, thank you for the great suggestion! The sedimentary facies analysis would be really useful for my research. Unfortunately, currently I don't have an access to the cores of the wells, but maybe in future work I can conduct the sedimentary facies analysis.

6. *There is no consistency between what is written in Paragraph. 2 (L.1 & 2), Page 46: "Usually, the alginite-rich layers pass gradually to the organic-rich siliceous rocks. This gradation gives the rocks a banded appearance under UV light" and in the title of Figure 4.1.2 (Page 46) "Photographs of the alginite-rich layers under white (a, c) and UV light (b, d) showing normal grading". Normal grading is used when coarse sediments grade upwards into progressively finer ones.*

Response: You right! Thank you! I changed "Photographs of the alginite-rich layers under white (a, c) and UV light (b, d) showing normal grading" on "…showing banded and graded appearance".

7. *Pelitic structure is not an appropriate (L2, Paragraph 2, Page 47) it means nothing in sedimentology.*

Response: Thank you for the correction! Changed on "lamination".

8. *What do you mean by: The specific morphology of the quartz of the alginite layers (paragraph 4 , L;6 & 7, 5.10 Depositional environment) It's necessary to describe this morphology.*

Response: I added some explanation in 4.7. Summary (Page 57): "Such abundance of quartz grains in the alginite-rich layers are not typical for the Bazhenov rocks. The quartz of host rocks are amorphous SiO_2, while quartz of the alginite-rich layers are crystalline. Amorphous SiO_2 formed from biological organisms (radiolaria or diatoms). The origin of quartz in the alginite-rich layers needs clarification."

9. *What do you mean by "eolian rafting"? (Paragraph 4, L8, 5.10 Depositional environment).*

Response: Sorry, it was mistype. I mean eolian processes.

10. *Marine basins, large lakes and swamps are sedimentary environments and not sedimentary facies. So it's recommended to replace in Paragraph 6, L.3, Conclusion, Page 87.*

Response: Thank you for the correction! Done.

Reviewer: Professor Sergey Stanchits

1. *The literature review part of thesis shows that type I kerogen has been found in the deposits related to various ages - from Paleozoic to the Cenozoic - in the USA, Canada, China, Spain, Australia and other countries. Are the findings, obtained on the basis of detailed analysis of Bazhenov Formation, applicable to other sedimentary basins of the globe?*

Response: Dear prof. Sergey Stanchits, thank you for the question! Indeed, organic matter characterized as type I kerogen has been found in various deposits. On the one hand, the finding, obtained on the basis of a detailed analysis of the Bazhenov Formation can be used for paleoenvironmental reconstruction in other sedimentary basins since these deposits all represent the selective accumulation of lipid-rich organic materials, on the other hand, each case must be approached individually since these organic-rich deposits can be formed in different deposition environment (marine, lacustrine or terrestrial). Probably, for same-age (Late Jurassic - Early Cretaceous) deposits the results of the research would be more applicable since this period represent the global distribution of black shales.

2. *In the "Conclusion" section, the author writes that the analysis of the proportion of type I kerogen may provide valuable information related to the prediction of expelled fluid properties. I assume that the readers of the thesis would be glad to know in a bit more details: what particular kind of important information can be obtained from the analysis of type I kerogen that can be applied to predict the properties of expelled fluid?*

Response: Thank you for the question! In nature, petroleum generated by the Bazhenov Formation would be a mixture of the liquids generated by each of its types of kerogen (type II and type I), which would change as thermal alteration progressed, as the various kerogen types reached their peak of generation. The properties of generated hydrocarbons by different types of the kerogen will differ. Type I kerogen will produce predominantly light (aliphatic) oils, while type II kerogen will generate also some aromatic compounds, according to research results. Hence, the results can serve to improve predictions of oil generation from the Bazhenov Formation.

3. *The author also writes that the analysis of type I kerogen may determine the source rock quality. Do the results of the presented study have any broader potential application? Is it possible to give at least some recommendations to improve the efficiency of the exploration and production of hydrocarbons?*

Response: According to the Rock-Eval pyrolysis studies, two types of unconventional reservoirs can be distinguished in the Bazhenov Formation [Spasennykh et al., 2021]. One is suitable for hydraulic fracturing, the other one is for thermal EOR. Studies showed that the first type corresponds to mature (MC2 catagenesis stage and more) rocks of the Bazhenov Formation, and the second one – immature

(PC3-MC1-2 catagenesis stages) organic-rich rocks. Therefore, knowing the thermal maturity of the Bazhenov Formation, we can most correctly choose the petroleum production method. The results of the PhD thesis show that the brightness of the luminescence of the alginite-rich layers makes it possible to quickly and easily without special time-consuming studies determine whether the Bazhenov Formation is thermally mature or immature.

The research results of the PhD thesis also have implications for studies of the changes in the chemical structure of kerogen as it matures, as well as for modeling oil generation processes. While choosing the parameters of the thermal EOR, it should be taken into account that the generation of hydrocarbons by type I kerogen requires higher temperatures than for type II kerogen.

The results also will be useful for analysis of the Upper Jurassic – Lower Cretaceous source rocks from other sedimentary basins to make inter-basinal and global correlations.

Spasennykh M., Maglevannaia P., Kozlova E., Bulatov T., Leushina E., Morozov N. (2021) Geochemical trends reflecting hydrocarbon generation, migration and accumulation in unconventional reservoirs based on pyrolysis data (on the example of the Bazhenov Formation), Geosciences, Vol. 11, No. 8. DOI: 10.3390/geosciences11080307.

Reviewer: Professor Nikolai Pedentchouk

1. *I found the section 5.10 "Depositional environments and origin" discussing possible mechanisms for the origin of type I kerogen in the Bazhenov Formation particularly interesting. However, there was not much of discussion comparing the mechanisms proposed for the Bazhenov Formation with those that we possibly offered in the previously published literature to explain the origin of type I kerogen deposits in the other sedimentary basins, i.e., in the Section 2.3 "Deposits containing type I kerogen". I suggest adding a paragraph or two at the end of Section 5.10 to cover this point.*

Response: Dear prof. Nikolai Pedentchouk, thank you for the suggestion! I added two paragraphs that explain the mechanism of the alginite-rich layers formation.

"Therefore, at least two types of kerogen can be distinguished in the Bazhenov Formation. The luminescent alginite-rich layers are very organic matter-rich (TOC 8.19 – 55.74 wt.%) and composed almost completely of alginites. The host rocks are organic-rich silicites (TOC 6.24 – 15.76 wt.%) with predominance of bituminite. Alginite can be derived from different organisms, e.g. green algae, dinoflagellates, cyanobacteria or bacterial mats. Due to thin walls of the alginites, microscopy cannot further resolve the kerogen origin. The high H/C ratios (up to 1.88) and high HI values (769 – 1053 mg HC/g TOC) in the alginite-rich layers indicating presence of hydrogen-rich type I kerogen. The H/C (1.09 – 1.19) ratio and HI (485 – 718 mg HC/g TOC) in the host rocks are also high, but lower than to the alginite-rich layers. The organic matter of the host rocks classifies as type II kerogen. Both types of kerogens are depleted in ^{13}C ($\delta^{13}C_{org}$ varies from –30.5 to –32.2‰, Table 5.8.1). The low values of $\delta^{13}C_{org}$ (from –30.5 to –32.2‰) for both types of kerogen indicate the preferential preservation of ^{13}C-depleted lipid derivatives in reducing environments, which in line with low Pr/Ph ratios < 1 (Table 5.6.1). The relatively higher $\delta^{13}C$ values of n-alkanes (Figure 5.9.1; Table 5.9.1) for the alginite-rich layers in comparison to the host rock may indicate derivation from organisms growing in more ^{12}C-depleted waters. Sulfur contents are slightly higher in the host rocks than in the alginite-rich layers. Almost all sulfur is present in framboidal pyrite (Figure 4.5.1). The ^{34}S-depleted pyrite of the host rocks ($\delta^{34}S_{tot}$ from –17.3 to –29.0‰) suggests anoxic conditions, while the alginite-rich layers show higher $\delta^{34}S_{tot}$ values from –6.0 to –18.5‰ indicating slightly more oxygen-rich conditions.

Interesting information is derived from nitrogen data in combination with carbon and nitrogen elemental composition. For the alginite-rich layers the C/N ratios and $\delta^{15}N_{tot}$ are very high compared to the host rocks (Table 5.8.1). As was mentioned above (5.8 Section) denitrification and/or NH_3 volatilization of organic material was leading to a strong positive excursion of $\delta^{15}N_{tot}$ values and loss of nitrogen. Thereby, it can be assumed, that the algae grew and lived in oxic waters of the Bazhenov paleosea and after burial, the diagenesis continued in the anoxic environment where denitrifying bacteria decomposed part of the microbial mats leading to high C/N ratios and $\delta^{15}N_{tot}$ values (Figure 5.10.2)."

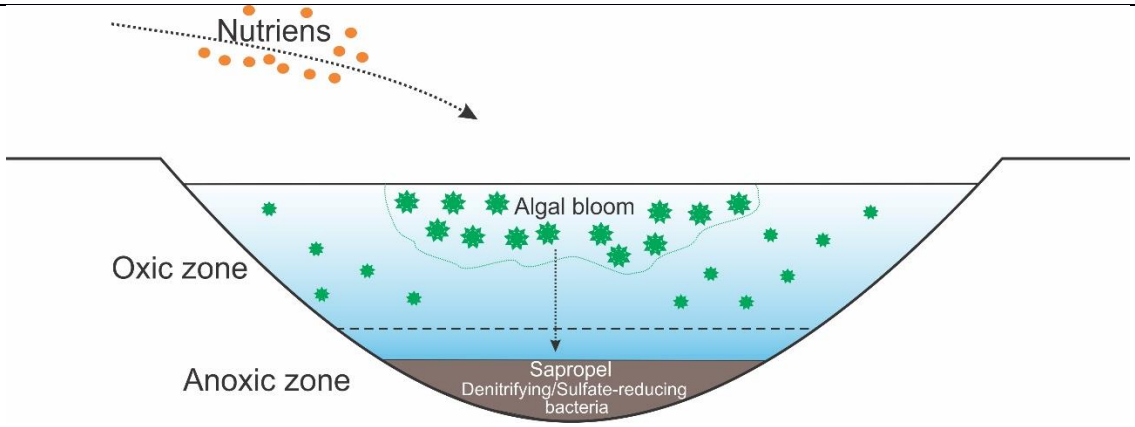

Figure 5.10.2. Schematic illustration showing the mechanism of the alginite-rich layers formation

2. *"The majority of petroleum source rocks for oil fields." This looks like a phrase, not a sentence.*

Response: Thank you! Corrected.

3. *"had undergone", or had not undergone?*

Response: Thank you for the correction. I improved the text.

4. *Who are "we"? Better use a singular pronoun or a passive form, as the thesis is supposed to represent you individual effort.*

Response: Thank you! Corrected. "In this work, a detailed study of the discovered in the Bazhenov Formation luminescent layers containing pure type I kerogen is presented."

5. *Was it just speculation or were their any data used to support those statements about the presence of Type I kerogen in the BF?*

Response: Thank you for the question! Goncharov and co-authors indicated type I kerogen in the Bazhenov Formation based on the Rock-Eval pyrolysis data (high hydrogen index and T_{max}) and kinetics (narrow Ea distribution) [Goncharov et al., 2016]. But in this work, they did not provide a detailed characterization of the samples (for example, lithological features or maceral composition). Oksenoyd and co-authors suggest type I kerogen based on Rock-Eval pyrolysis data plotted on the modified van Krevelen diagram [Oksenoyd et al., 2017]. Kontorovich and co-authors showed that only a few samples of the Bazhenov Formation belong to types from transitional kerogen type II to I based on elemental analysis of isolated kerogens [Kontorovich et al., 2019].

Goncharov I.V., Samoilenko V.V., Oblasov N.V., Fadeeva S.V., Veklich M.A., Kashapov R.S., Trushkov P.V., Bahtina E.S. Types of organic matter and catagenesis of the Bazhenov formation and its same-aged analogues // Oil Ind. 2016. Vol. 10. pp. 20–25.
Oksenoyd E.E., Volkov V.A., Oleynik E.V., Myasnikova G.P. Kerogen types of Bazhenov Formation based on pyrolysis data and their comparison with oil parameters // Oil and Gas. 2017. Vol. 5. pp. 34–43.
Kontorovich, A.E., Bogorodskaya, L.I., Borisova, L.S. et al. Geochemistry and catagenetic transformation of kerogen from the Bazhenov horizon // Geochem. Int. 2019. Vol. 64. No 6. pp. 621–634. DOI:10.1134/S0016702919060028.

6. *Same comment as above about "extensive bacterial reworking in a reducing environment".*

Response: Thank you for the correction. I improved the text.

7. *What about lacustrine basins?*

Response: Thank you! Yes, lacustrine basins too. Corrected.

8. *Better to say "higher terrestrial plants".*

Response: Thank you! Corrected.

9. *Better make it more specific, i.e. that it is "sedimentary organic matter".*

Response: Thank you! Corrected.

10. Here and throughout the thesis, be more specific with regard to what is meant by "our own laboratory studies". *What* laboratory/organisation?

Response: Thank you for the correction. I improved the text.

11. *"Our own"?*

Response: Thank you for the correction. I improved the text and figure.

12. *"heterotrophic"?*

Response: c

13. *Did they provide any explanation for this observation?*

Response: The authors associate the ^{15}N-enrichment of kerogen with several processes. The nitrification would tend to increase ^{15}N in ammonium and denitrification would increase ^{15}N in nitrate. Together, these processes would enhance ^{15}N enrichment associated with volatilization of ammonia during the deposition of the Green River shales.

14. *These $d^{13}C$ values are extremely high! Could there be any other explanation for such values in addition to the role of global glaciation and drawdown of CO_2? For example, the contribution of green sulphur bacteria, that produces biomass with the $d^{13}C$ values in this range?*

Response: Thank you for the question! The changes in carbon isotope fractionation as a result of plankton evolution or changes in the dominance of a particular phytoplankton group cannot be eliminated completely, but such changes were not reported by the authors [Simoneit et al., 1993]. The authors mentioned the physiological specialties of Tasmanites such as cell size and growth rate, which can also lead to ^{13}C enrichment.

Simoneit B.R.T., Schoell M., Dis R.F., Radler de Aquino Neto F. Unusual carbon isotope compositions of biomarker hydrocarbons in a Permian tasmanite // Geochim. Cosmochim. Acta. 1993. Vol. 57. No 17. pp. 4205–4211. DOI: 10.1016/0016-7037(93)90316-O.

15. *Check spelling. It should be "Simoneit"*

Response: Thank you! Corrected.

16. *Specify what each of these abbreviations stands for (PDB, AIR, CDT).*

Response: Thank you! I improved the text.

17. *This sentence does not make sense. The n-alkanes are first converted into CO2 in the oxidation reactor at 1000C and then the CO2 gas is analyzed (by ionization in the ion source) in the mass spectrometer where m/z 44, m/z 45, and m/z 46 are generated by electron impact ionization.*

Response: Thank you for the correction!

18. *It is very difficult to see any text in the figure 3.2.4. Either add labels or enlarge the figure so that the reader could see what is going on.*

Response: Thank you! The figure 3.2.4 was improved.

19. *Accepted classification of what? Be more specific.*

Response: Thank you! Corrected.

20. *"Stratification of the Bazhenov sequence" Or did you mean "Stratigraphy"?*

Response: Thank you! Corrected.

21. *How were these three characteristics (plasticity, flexibility, density) assessed? Which methods were used?*

Response: Thank you for the question! These characteristics of the alginite-rich layers were obtained during lithological examination in comparison to the host rocks (organic-rich silicites). There were no numerical determinations, but these characteristics are very different in the host rocks.

22. *Why so few data points in comparison with those shown in a)?*

Response: Dear prof. Nikolai Pedentchouk, figure 5.2.1b shows the data obtained from elemental analysis of isolated kerogens. For this research, only a few samples were chosen for kerogen isolation since this very time-consuming technique. Meanwhile, Rock-Eval pyrolysis is a more labor-saving and also very useful method.

23. *"to be elated yet." a typo?*

Response: Thank you! I mean here "eluated", but I think "expelled" would be more correct.

24. *Do you mean the identification of the source and/or environment of deposition of OM?*

Response: Yes, thank you! Corrected.

25. *Better say "higher d15N values".*

Response: Thank you! Corrected.

26. *Figure 5.8.2. Put publication years in parentheses.*

Response: Thank you! Corrected.

27. *Just say "usually are 12C-enriched".*

Response: Thank you! Corrected.

28. *Where does this information come from? Was is published?*

Response: Yes, it was published by Liu and co-authors.

Liu Z., Moldowan M., Nemchenko-Rovenskaya A., Peters K. Oil families and mixed oil of the North-Central West Siberian basin, Russia // Am. Assoc. Pet. Geol. Bull. 2016. Vol. 100. No 3. pp. 319–343. DOI:10.1306/12111514199.

29. *Remind the reader what kerogen type characterizes the host rock.*

Response: Thank you! Improved.

30. Need to add a statement here about what you learned from compound-specific n-alkane d13C data.

Response: Thank you for the suggestion! I added statement in the Section 5.11. "The moderate correlation of isotopic trends for individual n-alkanes suggests that extractable organic matter of the alginite-rich layers and the host rocks is derived from the similar biological source. At the same time, the relatively lower $\delta^{13}C$ values of n-alkanes for the host rocks may indicate derivation from organisms growing in deeper, ^{13}C-depleted waters."

31. Why are the references numbered? Arranging them in the alphabetical order should be sufficient.

Response: Thank you! Improved.

32. "Pedentchouk N., Turich C. No Title" Why not?

Response: My apologies. Corrected.

Reviewer: Professor Alexei Tchistiakov

No corrections requested.