Skoltech
Skolkovo Institute of Science and Technology

Thesis Changes Log

Name of Candidate: Nadezhda Khaustova

PhD Program: Petroleum Engineering

Title of Thesis: Uranium accumulation in marine source rocks: role of redox conditions and correlation with productivity

Supervisor: Professor Mikhail Spasennykh

Co-supervisors: Professor Yuri Popov

Dr. Elena Kozlova

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

Doctoral Thesis: Nadezhda Khaustova
Title: Uranium Accumulation in Marine Source Rocks: Role Of Redox Conditions and Correlation With Productivity

Dear Jury Memebers

I sincerely thank you for the careful reading of the thesis and valuable comments. I carefully addressed all issues and answered them below, point-by-point, with the reviewers' comments.

Reviewer: Professor Devendra Narain Singh

Abstract

1. The type of studies conducted (experimental, numerical, or both) shall be mentioned.

Response 1: Thank you for the comment. I corrected the abstract the suggested way and added the next comment: "The experimental and numerical research methods were used in this paper."

2. It is mentioned as 'other' in the factors influencing uranium accumulation. Clarify.

Response 2: Thank you for your constructive suggestion. I corrected the sentence in the suggested way and clarified it in the next way: "The research allows us to clarify the main factors affecting uranium accumulation in marine source rocks, including the concentration of uranium in sea water, accumulation of uranium in marine organisms, uranium sorption (U^{+6}) by organic matter (depending on Eh, pH), the precipitated organic matter type (sapropelic, humic), continental run-off and sedimentation rate, redox conditions, mineral composition of rocks and presence of phosphates, also diagenetic and catagenetic processes."

Chapter 1: Introduction

1. What is the reason for considering uranium for characterizing the oil source rock?

Response 1: Thank you for the comment. Oil source rocks are widespread formations throughout the world. These rocks are characterized by increased concentrations of P, U, Mo, V, As, Zn, Cu, Ni, Ag, Au, and some other chemical elements [Neruchev, 1982; Yudovich and Ketris, 1988]. Gamma-ray spectral logging records total radioactivity, and concentrations of uranium, thorium, and potassium and is included in the standard well logging methods list. The uranium content characterizes the anoxic conditions and the organic carbon present in rocks [Dobrynin, 1991]; also uranium concentration is used for the identification of source rock lithological boundaries, well-to-well log correlation (in combination with other logging data), as well as for core-to-log data integration. My research objective was to expand the uranium distribution and content used to solve various geological and geophysical problems. The literature review showed that the distribution and concentration of uranium carry a large amount of information for characterizing the section of oil source rocks.

2. It is mentioned that data was obtained on core samples from 13 wells but only data for 9 wells is provided. The data for the remaining 4 wells shall be included.

Response 2: Thank you for your comment and your consideration. The uranium content and distribution, and pyrolysis data are available for 13 wells of the Bazhenov Formation. Appendix A presents the uranium content and distribution results, organic matter concentration, and distribution based on the thermal core logging results, and U/TOC ratio only for 9 wells, since the organic carbon measurement by thermal core logging was carried out only for 9 wells of the Bazhenov Formation.

Chapter 2: Review of Literature

1. The reason for the higher mobility of uranium during weathering shall be specified.

Response 1: Thank you for your interesting question. I have explained it in my main text.
According to the literature data [Roslyakov et al., 2014], the uranium behavior in the processes of rock weathering is determined by its high migration ability in an oxidizing environment. An important geochemical uranium feature is the U^{4+} ability to easily oxidize from the U^{4+} to the U^{6+}. U^{6+} is usually represented by the uranyl ion UO_2^{2+}, which forms various salts with acids. The easy sulfate and carbonate solubility of uranium compounds U^{6+} play an exceptional role in the migration and uranium concentration during weathering. The most widespread uranium migration form is uranyl-carbonate and uranyl-humate complexes.
The uranium removal from rocks significantly outstrips their deep chemical change. The weathering of rocks in an oxidizing environment leads primarily to a change in the uranium occurrence forms. Uranium concentrated in rock-forming and accessory minerals goes into solution with subsequent sorption by finely dispersed oxides and silicates. There is a mobilization and concentration in the process of easily mobile uranium weathering, and sorption associated with clay minerals and hydroxides.

2. It is mentioned that the transition of U^{+6} to U^{+4} depends on pH and Eh. Is there any effect of pressure and temperature conditions in this transition?

Response 2: Thank you for your interesting question. The behavior of water-soluble uranium is largely controlled by the pH and Eh, as well as by the hydrogen sulfide concentration.

3. It is mentioned that the anaerobic scheme of organic matter decomposition takes place at low Eh values. A range shall be mentioned from the literature studies.

Response 3: Thank you very much for your question. In the literature source [Kizil'shtejn and CHernikov, 1999]: Eh in anoxic conditions vary in the range from +50 mV ÷ -150 mV (in more wide range +115 mV ÷ -450 mV). Also, in the other literature source [https://www.ecounit.ru/artikle_105.html]: Eh in anoxic conditions is characterized by values < 0 mV.

4. The depth of various zones presented in Figures 5 and 6 shall be included.

Response 4: Thank you for the comment. Figures 5 and 6 are schematic and the schemes in the article [Demaison and Moore, 1980] were not indicated, only the marine sediments thickness (100 cm). However, I can guess the depths based on the study of the Arctic marine sediments (oxic conditions) and the Black Sea sediments (anoxic conditions).

5. The explanation on what is V I Vernadsky assumption shall be provided.

Response 5: In the Vernadsky research [Vernadskij, 1934], in the chapter "On the Concentration of Radium in the Biosphere by Living Organisms" it is emphasized that: "The ability to live organisms to concentrate radium is of great importance in the biosphere structure. Attention was also paid to the study of the concentration of the chemical elements in living organisms in comparison with their average content in the organism's living environment. This phenomenon is of much greater importance since living organisms concentrate not only on radium but also on many other radioactive elements. Organisms concentrate potassium. Uranium is collected on organogenic part of the organisms." This information was added to the thesis.

6. In figure 9, the sedimentation rates are qualitatively mentioned. The quantification of slow, high, and maximum sedimentation rates shall be included.

Response 6: Thank you for your comment. According to sedimentation rates classification:

Table 1. Sedimentation rate classification

Type	Sedimentation rate, cm/year
Extremely low	0.00001÷0.0001
Very low	0.0001÷0.001
Low	0.001÷0.01
Moderate	0.01÷0.1
High	0.1÷1.0
Very high	1.0

So, I can conclude according to Table 1 and the literature review [Zanin et al., 2016] that the low sedimentation rate in the Bazhenov Formation is 0.0004÷0.0006 cm/year, the high sedimentation rate is 0.1÷1.0 cm/year and maximum sedimentation rate is 1.0 cm/year. I have changed Figure 9 in the thesis.

7. Why phosphate enriched organic matter adsorbs more uranium?

Response 7: Several researchers have analyzed uranium forms bonding with fish skeletons' apatite (phosphates). According to one of them [Chencov, 1956], the uranium enters the apatite crystal structure in a tetravalent form, isomorphically replacing calcium. There is also another point of view [Kochenov et al., 1973]: during bone tissue fossilization, it is possible to release tetravalent uranium in the form of a solid phase - uraninite, obviously sorbed by the phosphate mineral.

8. In the second figure of Figure 13, why the uranium concentration decreases at the same Eh value? In the text below, it is mentioned that organic matter concentration changes

from 5 to 10% when Eh changes from 200 to -120mV. But the figure shows otherwise. Clarification is required.

Response 8: Thank you for your correction. I have given more explanation: «When Eh changes from -200 to -120 mV, when moving from sharply reducing to less reducing conditions, the organic matter concentration decreases by half because of its bacterial oxidation (from 10% to 5%)».

9. From the literature review, how it is concluded that the influence of the redox condition on uranium accumulation is maximum or dominant?

Response 9: According to Neruchev's research [Neruchev, 2007], it is not black shales are a factor in uranium accumulation, but, on the contrary, uranium is a factor in the black shales formation and, at the same time, major evolutionary rearrangements of the biosphere. However, this is a highly controversial opinion.
As an example from a literature review [Ketris and YUdovich, 1988], the carbonaceous sediments of the Pettaquamscoot Estuary (Rhode Island, USA) provide an example of modern uranium accumulation and a possible model for a similar process for ancient black shales. The estuarine system is represented by two brackish lakes separated by a shallow barrier. The waters of the Atlantic Ocean penetrate the bottom parts of the lakes, resulting in an oxygen-free environment. Organic matter accumulates (TOC=1-15%), sulfate reduction develops; sediments are enriched in uranium (from 5-20 ppm). This example shows the full reality of the uranium accumulation in the sediments of the hydrogen sulfide facies at background concentrations of uranium in sea water. The decisive role was played not by the uranium concentration in sea water, but by hydrogen sulfide contamination, which contributes to the effective uranium sorption by organic matter. The same behavior and uranium accumulation is characteristic of the Black Sea sediments. Moreover, this once again proves that redox conditions have a decisive influence on uranium accumulation.

Chapter 3: Uranium accumulation in marine sediments under different redox conditions on the example of the White, East Siberian, and Black Seas, as well as the Laptev Sea

1. The criteria for selection of the sites that have been studied shall be included.

Response 1: Thank you for your comment. I have added the next sentence in the thesis: «The sampling stations were selected within the limits of different facies zones identified based on sub-bottom profiling and the different water depth».

2. There is no constant interval of depth where the concentrations of elements are recorded except for stations 2, 3, 4, 5, and 6. What is the reason for the varying intervals?

Response 2: Thank you for your comment. If we talk about station 1, then one «11th» sample was not enough for the ICP-MS study, so there are differences in the sampling interval.
If we talk about the 7th and 8th stations of the Black Sea, then, unfortunately, it was not possible to measure the concentrations of the chemical elements by the ICP-MS method. The 7th station of the Black Sea is characterized by more reducing conditions compared to the 8th station; therefore, more samples were taken for the elemental composition study for the 7th station.

3. What is the reason for terminating the recording at variable depths at different stations?

Response 3: Thank you for your question. I would like to apologize, but I did not understand your question.

4. The variation of uranium for the studied stations is very less. Is there any major effect even with the very small increase in uranium concentration?

Response 4: Thank you very much for such an interesting question. Of course, the main factor influencing the change in the uranium concentration in studied stations, even a significant change, is associated with a change in redox conditions.

5. The term isotopy in figures 24 and 25 shall be changed to isotopic.

Response 5: Thank you for your comment. I have changed it**.**

6. It is mentioned in Pg. 73 that high isotopic sulfur corresponds to oxidizing conditions in the Laptev Sea. But in the case of the black sea, it is written that positive values of isotopic sulfur reflect an increase in sulfate reduction intensity. Is it not contradictory?

Response 6: Thank you for your important comment. Of course, it is contradictory; I did not formulate my main idea in the right way. I have rewritten and given a more clear explanation: «The Black Sea bottom sediments upper part is characterized by negative $\delta^{34}S$ values, but the bottom part of the Black Sea sediments is characterized by positive $\delta^{34}S$ values with depth. The cyclicity of changes in redox conditions is shown in the Black Sea sediments (station 7) since below 200 cm the $\delta^{34}S$ values are the same as for the upper part of the sediment: "lightening" and again "heavier" isotopic composition. According to the results of sulfur studies, the Black Sea sediments accumulated in a more reducing environment with more significant variations in redox conditions and the sulfate reduction intensity than the White and the Laptev Seas sediments».
In addition, I have corrected the conclusions in Chapter **C, N, S Isotope Composition**: «The general trend of the sulfur isotopic composition behavior in the Black Sea sediments: an increase in $\delta^{34}S$ values with depth is observed. Negative $\delta^{34}S$ values indicating sulfate reduction with the development of reducing conditions in the upper layers of the Black Sea sediments are replaced by positive values indicating oxidizing conditions, and the same thing is repeated in the underlying layers (negative are replaced by positive values $\delta^{34}S$)».

7. The axes of the graph in figure 32 shall be interchanged because the deposition of thorium is dependent on clay minerals but the graph infers otherwise.

Response 7: Thank you for your comment. I have changed the graph on the Figure.

8. It is mentioned that uranium concentration was up to 35 ppm. But nowhere in the graph or figures, has the uranium content reached this value. Clarification is required.

Response 8: Thank you for your comment. The literature review in Table 27 is indicated that the uranium concentration reaches 35 ppm in the ancient Black Sea sediments.

9. More details on how thermodynamic modeling like governing equations shall be provided.

Response 9: Thank you for your suggestion. I have added the formula for calculation of the partial pressure of oxygen – this data and other (Eh, pH, and the initial uranium concentration in pore water) used for the uranium speciation calculation and the uranium distribution between the aqueous phases and solid uranium phases (minerals) along the bottom sediment column.

Chapter 4: Distribution of uranium (U) and uranium/TOC (U/TOC) ratios in the unconventional reservoir on the example of the Bazhenov Formation

1. What are the porosity and permeability values of BF rocks?

Response 1: Thank you for your question. The porosity K_p = 4÷12 % and permeability K_{pr} = 0.02 ÷ 2.7 md for natural reservoirs in BF rocks. The porosity K_p < 2 % and permeability K_{pr} < 0.01 md for promising for development using reservoir stimulation intervals in BF rocks [Kalmykov and Balushkina, 2017].

2. It is mentioned that 13 wells were studied in the Bazhenov Formation. Only data for 9 wells were provided. Clarification is required for the absence of data for 4 wells and a U/TOC diagram is presented for samples from 11 wells. Why this irregularity is occurring?

Response 2: Thank you for your comment and your consideration. The uranium content and distribution, and pyrolysis data are available for 13 wells of the Bazhenov Formation. Appendix A presents the uranium content results, organic matter concentration based on the thermal core logging results, and U/TOC ratio only for 9 wells since the organic carbon measurement by thermal core logging was carried out only for 9 wells of the Bazhenov Formation. In addition, it was possible to create the cross-plots and diagrams in Figures 54, 60, and 63 only for 11 wells of the Bazhenov Formation due to incomplete pyrolytic data for two studied wells out of thirteen wells.

3. In figure 47, there is no isotopic sulfur variation presented. But in the figure description, it is included. It shall be removed.

Response 3: Thank you for your corrections. I have changed it in the figure description: «Figure 47. Logviews BF: U-core (gamma spectrometry); TOC – organic matter profile with 1 mm resolution (TCP); ratio U/TOC; deposition environment: sub-anoxic, anoxic, sub-oxic. »

4. It is given that at U/TOCmax<U/TOC, the deposition environment is anoxic. But subsequently, it is mentioned that sub-anoxic and anoxic environments characterize low uranium concentration. Is it not contradictory?

Response 4: Thank you for your correct comment. Of course, anoxic conditions are characterized by high uranium and organic carbon concentrations, while oxic deposition environments are characterized by low uranium and organic carbon values. Nevertheless, the intervals in the section of well 5 in Figure 47 with transitional deposition environments can be characterized by variations in the uranium and organic carbon concentration. For example, for well 5, these intervals are characterized by organic carbon variations from the minimum to the maximum, and the uranium concentration values are closer to the minimum. I have corrected it in the thesis.

5. What is the significance of V/Mo and V/Cr ratios in studying redox conditions?

Response 5: Thank you for your question. According to the literature review and the getting results studying the Bazhenov Formation:

Parameter	Oxic conditions	Anoxic conditions
V/Mo	• 10-60 (Red Sea black shales) [Baioumy and Lehmann, 2017] • ≈ >7 (Bazhenov Formation)	• < 2 (Red Sea black shales) [Baioumy and Lehmann, 2017] • ≈ < 7 (Bazhenov Formation)

V/Cr	• < 2 (Devonian-Mississippian black shales, USA) [Rimmer, 2004] • ≈ < 13 (Bazhenov Formation)	• > 4.25 (Devonian-Mississippian black shales, USA) [Rimmer, 2004] • ≈ > 13 (Bazhenov Formation)

Reviewer: Professor Dmitry Koroteev

1. I would like to see a more detailed discussion on how the results (e.g. ones summarized in the table 34) could help the reservoir engineers to plan the potential field development in the areas studied by Nadezhda. I would also like to read more considerations about applicability of the studies done by Nadezhda to other formations worldwide.

Response 1: Thank you very much for the interesting question. To date, the following shale oil production technologies exist:
1. Multi-stage hydraulic fracturing
2. In-situ combustion
3. Thermal simulation.
These technologies apply to oil production from the Bazhenov Formation. Before planning the development technology of a shale oil field, it is necessary to conduct a complex of geological, geophysical, and geochemical studies to determine the reservoirs, interlayers, and depths to which a certain development technology is suitable.
The technique proposed by us makes it possible, using the spectrometric gamma method (uranium concentration distribution in depth) and continuous profiling of thermal properties on the core (TOC concentration distribution in depth) or pyrolysis (TOC concentration distribution in depth) data to identify intervals. In addition, propose for certain intervals development technologies according to the classification given in the thesis (Table 34).

All analysis of the uranium concentrations together with pyrolytic data for the Bazhenov Formation rocks, which I perform in my research, can be repeated for the other unconventional reservoirs rocks (Eagle Ford, Baken Formations, and others). In my opinion, it will be the same logical idea and type classification, but with different uranium and TOC concentration values.

2. I would add a graphical representation of the importance of various factors influencing the uranium concentration and productivity to the conclusion.

Response 2: Thank you for the comment. In the thesis text and the Conclusion, I tried to explain the deposition environments and the factors influencing uranium concentrations for different type intervals described in Table 34. I have added the information about factors of uranium accumulation in Table 34.

Reviewer: Professor Ksenija Stojanović

1. Table of content – please uniform the style: Capitalize the first letter in all words in titles of chapters (e.g. Review of the Literature, Materials and Methods, etc.) or capitalize the first letter in the first word only (e.g. Objects of research, Role of redox conditions in uranium accumulation in source rocks, etc.) and of course names of seas and formation, as it has been already performed.

Response 1: Thank you very much for your comment. I have improved it in the thesis.

2. Page 80; Line 8 from the top: carbon instead of carbom

Response 2: Thank you for your comment. I have corrected this mistake.

3. Page 93; Line 5 from the top: Braduchan и др., 1986 should be replaced by Braduchan et al., 1986.

Response 3: Thank you for your comment. I have corrected this mistake.

4. Page 112; Line 15 from the top: Formula of pyrolusite is MnO_2. Therefore you should correct the sentence: Increased uranium content is associated with uranium concentration by phosphate minerals (represented by P_2O_5 content) and manganese (represented by MnO). Analogically the word "pyrolusite" should be removed from line 18 at the same page.

Response 4: Thank you for your comment. I have corrected this mistake.

5. Appendix A; Table 36; the first row and the first column: epth should be corrected into Depth.
er

Response 5: Thank you very much for your comment. I have improved it in the thesis.

Reviewer: Professor Sergey Stanchits

1. I deem that, based either on the results of the performed studies or literature review, in the PhDthesis it is worth to indicate whether the native uranium mineral phases were observed in BazhenovFormation or not. If yes – what are they related to?

Response 1: Thank you for the comment. The study of the uranium distribution features in the rocks, carried out by the fission radiography (f-radiography) method [Rihvanov et al., 2019] indicates the three-occurrence forms of existence of this element (in a terrigenous matrix, local organic matter accumulations, and shell valves). Uranium is mainly sorbed by shells and dead organism remains [Pluman, 1971; Shchepetkin et al., 1984]. The uranium's own mineral phase's existence was established during electron microscopic studies [Rihvanov et al., 2019]. It has been established that uranium's mineral phases are confined to the calcium phosphate mineral phases, uranium minerals have a random distribution, and are represented by their mineral species in the coffinite form and uranium oxide.

2. I have found that in the "Bibliography" section Russian letters are used many times, for example,"и др.". I recommend either including the list of all coauthors, or writing "et al." Also, the sentence"Том 1 [Электронный ресурс]" should be translated into English.

Response 2: Thank you very much for your comment. I have improved it in the thesis.

Reviewer: Professor Nikolai Pedentchouk

Abstract

1. Not sure what this refer to. "Oil saturation" of what?

Response 1: Thank you for the comment. I have improved it in the thesis.

2. What is considered "high" here? What %TOC values are you referring to?

Response 2: Thank you for the comment. The %TOC values are more than 8%.

3. What are broader implications of this research? Are the results applicable only to the BF?

Response 3: Thank you for your question. In this research, I tried to classify and characterize the oil-source rocks in the example of the Bazhenov Formation according to the uranium concentration. The approach proposed in my study can be used to classify other unconventional reservoir rocks by uranium content.

Introduction

4. Needs a reference: «reaching values above 100 ppm»

Response 4: Thank you for the comment. I have improved it in the thesis.

Review of the Literature

5. Instead sorb – sorbed

Response 5: Thank you for the comment. I have improved it in the thesis.

6. Referencing style? Do you really need to give http:// link here?

Response 6: Thank you for the comment. I have improved it in the thesis.

7. Needs a reference: «Redox conditions are the most important physical and chemical characteristics…».

Response 7: Thank you for the comment. I have improved it in the thesis.

8. Font within the Figure 4 is difficult to read.

Response 8: Thank you for the comment. I have improved it in the thesis.

9. May need explanation for those not familiar with this convention: « clarke uranium concentration».

Response 9: Thank you for the comment. I have improved it in the thesis.

10. May also might need a brief reminder what these are for those not familiar with the difference: « sapropelic vs. humic)»

Response 10: Thank you for the comment. I have improved it in the thesis.

11. It shows theres correlation, but it is not the same as causation, or "influence": «Theoretical distribution of humic and sapropelic materials, accumulating organic matter, estimated uranium and oil content in a shallow sea are presented in *Figure 8*. This scheme shows us that different combinations of humic and sapropelic organic matter and the organic matter content (TOC) influence the uranium concentrations».

Response 11: Thank you for the comment. I have improved it in the thesis.

12. What is considered to be "slow", "high", and "maximum" in terms of sedimentation rate?

Response 12: Thank you for your comment. According to sedimentation rates classification:

Table 1. Sedimentation rate classification

Type	Sedimentation rate, cm/year
Extremely low	0.00001÷0.0001
Very low	0.0001÷0.001
Low	0.001÷0.01
Moderate	0.01÷0.1
High	0.1÷1.0
Very high	1.0

So, I can conclude according to Table 1 and the literature review [Zanin et al., 2016] that the low sedimentation rate in the Bazhenov Formation is 0.0004÷0.0006 cm/year, and the high sedimentation rate is 0.1÷1.0 cm/year and maximum sedimentation rate is 1.0 cm/year. I have changed Figure 9 in the thesis.

13. What does it mean: «condensed compounds»?

Response 13: Thank you for your comment. Melanoidins are *condensation products* of amino acids with cellulose material.

14. Awkward. Needs rephrasing: «the selection of factors determining the uranium content and assessment of their influence complicates interpretation».

Response 14: Thank you for your comment. I have rephrased the sentence: The identified factors that determine the uranium concentration complicate the interpretation of the uranium concentration distribution in depth when working on each geological object.

Chapter 3

15. Not very clear what area of the Black Sea this insert represents (Figure 16).

Response 15: Thank you for the comment. I have improved it in the thesis.

16. What are the units here? How do classify "modern", "ancient" etc.? Remind the reader here as well (Table 13, word «Age»)

Response 16: Thank you for the comment. I have improved it in the thesis. The stratigraphic subdivision of the deep-water Holocene sediments of the Black Sea is carried out according to the marker lithological horizons, first identified by A.D. Arkhangelsky and N.M. Strakhov (Arhangel'skij and Strahov, 1939). Referring to the study Geochemistry of the Black Sea (Mitropol'skij, Bezborodov and Ovsyanyj, 1982) - the upper (0-10 m) stratum of bottom sediments of the Black Sea is stratigraphically subdivided into modern, ancient, and Novoeuxinian sediments.

17. Here and throughout the thesis, don't use isotope jargon, i.e. "light" vs. "heavy". Say 34S-depleted vs. 34S-enriched instead: "lightening" and again "heavier" isotopic composition

Response 17: Thank you for the comment. I have improved it in the thesis.

18. What about the other seas studied, as described above: « In contrast with the White Sea»?

Response 18: Thank you for the comment. I have changed it in the thesis: « In contrast with the Arctic Seas…».

19. What is considered to be "ancient": « Ancient Black Sea sediments »?

Response 19: Thank you for the comment. I have improved it in the thesis. The stratigraphic subdivision of the deep-water Holocene sediments of the Black Sea is carried out according to the marker lithological horizons, first identified by A.D. Arkhangelsky and N.M. Strakhov (Arhangel'skij and Strahov, 1939). Referring to the study Geochemistry of the Black Sea (Mitropol'skij, Bezborodov and Ovsyanyj, 1982) - the upper (0-10 m) stratum of bottom sediments of the Black Sea is stratigraphically subdivided into modern, ancient, and Novoeuxinian sediments.
Ancient Black Sea sediments (**located under modern sediments, Holocene**) are represented by grey clayey silt and black sapropel silt, and the content of the hydrotroilite is 0.01–0.03%. Organic matter concentration is in the range of 0.22%–8.95%, uranium concentration is 1.1 ppm–35 ppm, the average values of the U/TOC ratio vary from 0.96 to 2.83 ppmU/% TOC, and Eh values vary from −220 mV to −80 mV.

20. What are the age boundaries here (Table 27)?

Response 20: Thank you for the comment. I have improved it in the thesis. The stratigraphic subdivision of the deep-water Holocene sediments of the Black Sea is carried out according to the marker lithological horizons, first identified by A.D. Arkhangelsky and N.M. Strakhov (Arhangel'skij and Strahov, 1939). Referring to the study Geochemistry of the Black Sea (Mitropol'skij, Bezborodov and Ovsyanyj, 1982) - the upper (0-10 m) stratum of bottom sediments of the Black Sea is stratigraphically subdivided into modern, ancient, and Novoeuxinian sediments.

21. Figures 34 - 38 could be made larger. As it stands, some of the font within the figures is difficult to read.

Response 21: Thank you for the comment. I have improved it in the thesis.

Chapter 4

22. The legend is very difficult to read. Consider enlarging Figure 44.

Response 22: Thank you for the comment. I have improved it in the thesis.

23. Consider change the font size along the X- and Y-axes. Here and in the similar figures below (Figure 50 and 51).

Response 23: Thank you for the comment. I have improved it in the thesis.

Conclusion

24. Could redraw this figure 66 (make it "portrait" orientation so that the font becomes larger.

Response 24: Thank you for the comment. I have improved it in the thesis.

Bibliography

25. Formatting issues, e.g. why are references numbered? Why some titles are given using the upper case letters (21. Dudaev, 25. Fertl, etc.)?

Response 25: Thank you for the comment. I have improved it in the thesis.

Appendix A

26. Should the tables in the Appendix be named separately from those in the main text, e.g. Table A1, A2, etc.?

Response 26: Thank you for the comment. I have improved it in the thesis.