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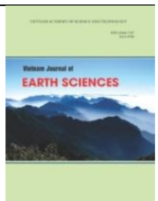


# Correlation of trace element composition of oils and other caustobiolites with chemical content of different types of biota and the Upper, Middle and the Lower Earth's Crust

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ABSTRACT

The trace element (TE) content of oils is known to have a polygenetic character and to be inherited from an organic matter, surrounding rocks and from formation waters. The presence of some TEs indicates the involvement of the deep source, at least from the Lower Crust. However, these conclusions have a qualitative character. We present the results of the correlation analysis of TE content of oils with the chemical compositions of the Upper, Middle, and Lower Crust, with different types of organic matter, clays, and causetobiolites. A logarithmic instead of a linear scale for TE concentration values is used in calculations because the examining values change by several orders of magnitude. The TE compositions of clays, coals, and shales correlate better with the composition of the upper continental crust and an organic matter. In contrast, the TE contents in the majority of oils correlate stronger with the Lower crust, which indicates a significant contribution from the Lower continental crust. This finding points to the role that the uprising flow of fluid plays in the process of the formation of oil. Only young oils from Kamchatka and from White Tiger huge oil fields indicate a better correlation with the Upper crust. This finding is explained by the lower depth of formation of the uprising flow of deep waters because of higher deep temperatures in Kamchatka and in the White Tiger oil field area. The obtained trend of change of TE content in clays and different caustobiolites oils including is interpreted as a mixing line between the subsurface end member (which is characterized by high correlation with the chemical content of the Upper crust and biota) and the deep end member (high correlation with the chemical content of the Lower crust).

*Keywords:* polygenesis of trace element content in oils; trace element content of different caustobiolites; genesis of trace element content in oils.



## 1. Introduction

The process of generation of oil is a very complex process of combined effects of deep and near-surface factors. The evidence of the involvement of organic matter, surrounding rock, and formation water can be traced from the trace element (TE) composition in oils. In

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most cases, the TE are various metals (V, Fe, Ni, etc.). A major part of the TEs in oils is believed to be inherited from an organic matter, as indicated by a close relationship between the TE content in oils and the chemical composition of biological materials (Punanova, 2004; Babaev and Punanova, 2014, and many other). A significant part of the TE composition of oils is inherited from the host rocks and from formation waters. Some trace elements in oils distinctly characterize the deep source, located at least in the Lower crust (Gottikh, Pisotskii, 2010; Gottikh et al., 2008). The latest conclusion is based on the presence of TEs typical of the lower crust rocks, and by the existence of a positive Eu-anomaly, which is connected with the involvement of the deep fluids suggested to be intruded from the Lower crust (Taylor and McLennan, 1985).

However, the conclusions above have a qualitative character only; they do not allow carrying out the quantitative comparison between relative contributions from the Lower and the Upper crust as well as from an organic matter in the TE composition of oils. Besides, the role of various factors mentioned above can differ in different oil and gas-bearing basins, and in different tectonic conditions, these differences remain unexamined if only the qualitative examination is performed. Below, we will discuss these problems and examine TE composition data of oils from the main oil-and-gas bearing basins of Russia and from two specific oil fields. We correlate the TE content in oils with typical TE composition of different rock types and different types of biota. As specific cases, we will examine the TE composition of young oils from the Kamchatka Peninsula and from the huge White Tiger oil field in Vietnam.

## 2. Method and the data

The trace element composition of crude oils is the result of different processes. Trace elements of oils are known to be inherited from biological matter, deep fluids, and from host rocks (Punanova, 2004; Punanova, 2017; Punanova, Rodkin, 2019; and others). The genetic characteristics of oils are examined using a number of indicators such as the V/Ni concentration ratio, Eu anomaly, etc. However, these characteristics may change widely depending on the variation in the concentrations of individual elements, which depend on many different factors; thus, these characteristics are frequently unstable (Maslov et al., 2015; Delu et al., 2018). This limits the possibility of examination of oil genesis using data on TE content. The use of the characteristic that depends on all trace elements contained in oils can give more robust genetic characteristics. As a more stable characteristic, we use the coefficient of correlation that depends on all available TE concentrations. The coefficients of correlation between TE content of different caustobiolites (including oils) and concentrations of main and trace elements in different host rock types, in the Upper, Middle, and the Lower continental crust, and in different types of organic matter were calculated. The models of the chemical composition of different geo-reservoirs, such as the Upper, Middle and Lower continental crust (Taylor and McLennan, 1985; Rudnick and Gao, 2003), the chemical content of different types of organic matter (Bowen, 1966), and TE content in different caustobiolites and clays (Punanova, 2004; 2017) were used in the calculation.

The quantitative comparison of contributions of different sources in the TE composition of oils became possible after the significant increase in the amount of available analytical data on the TE content in different caustobiolites (including oils). Rapid progress was obtained mainly due to the use of an inductively coupled plasma mass spectrometry method (ICP-MS). This method enables a more precise analysis of a larger number of trace elements.

The concentrations of different trace elements in oils and other caustobiolites (coals and shales) in the Upper, Middle, and Lower continental crust, and in the organic matter differ by several orders of magnitude. In this case, it is suitable to use a logarithmic rather than a linear scale for comparison of concentrations of different elements. It is easy to see that if the linear scale were used, the information about the content of the majority of TEs with low concentration would be factually lost. The calculation of the correlation coefficients for log-scale TE concentration values was shown to be fruitful (Rodkin et al., 2016; Punanova, Rodkin, 2018); the same methodology is used below.

**3. Results**

We have analyzed the relation between TE concentrations in different caustobiolites (oils, coals, and oil and black shales) with concentrations of different elements in the Upper, Middle, and Lower continental crust (Rudnick and Gao, 2003) and in different types of organic matter. For the baseline of the chemical content of organic matter, we have used the typical chemical content of aquatic and terrestrial plants and animals (Bowen, 1966). In most of the similar examinations performed earlier, the comparison had only the qualitative character and was based upon the visual comparison of concentrations similar to that presented in Fig. 1. The quantitative comparisons were carried out, as a rule, using a linear scale and for a special group of elements, such as Ni/V, Al/Si, Si/(Si + Al + Fe), (Fe + Mn)/Ti, La/Yb and other; such comparisons depended on concentrations of only several TEs and were frequently unstable (Maslov et al., 2015; Delu et al., 2018; and others).

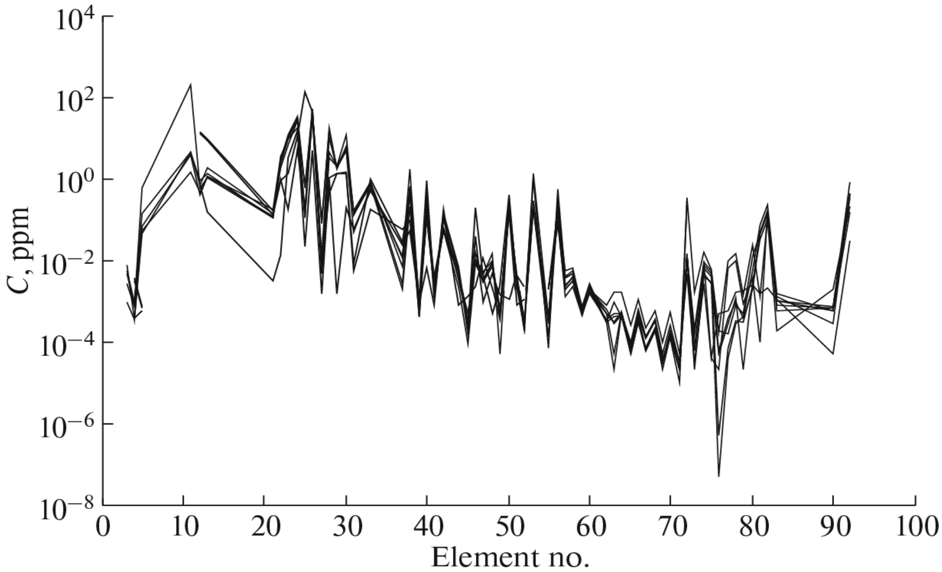


*Figure 1*. Variation in trace element concentrations in oils (C, ppm) from the Shaimsk region of West Siberia (from analytical data (Ivanov et al., 2007)). The samples appear to be similar

We present below the results of quantitative estimations calculating the correlation coefficient of TE contents using the logarithmic scale. As can be seen in the example shown in Fig. 2, there is a close correlation between mean TE compositions of oils and living matter. Similar correlations take part in other cases. It is also easy to see that if one uses a linear scale, the information about the concentrations of the majority of elements would be factually lost. In the presented case (Fig. 2), the correlation coefficient R between the logarithms of TE concentrations in the mean oil and mean biomass equals R = 0.56 for all elements with known concentrations. This coefficient is higher (R = 0.83) when the concentrations of only biogenic elements are used for calculations; the biogenic elements are those that are more abundant in living organisms, such as V, Ni, Fe, Co, Cr, Zn, As, Pb, Au, and Br (Rodkin et al., 2016). In both of these cases, however, the correlation has a similar statistical significance (the probability of finding such a correlation by chance is less than 1% in both of these cases). We believe that the estimations obtained with the use of information about all TEs are more robust, such estimations are used below. The robustness of the results of calculations was discussed in detail (Rodkin et al., 2016). The difference of several (2-3 up to 5) percent typically taking place for the cases of samples taken at similar conditions can be considered as suitable to consider the results of calculations as robust.

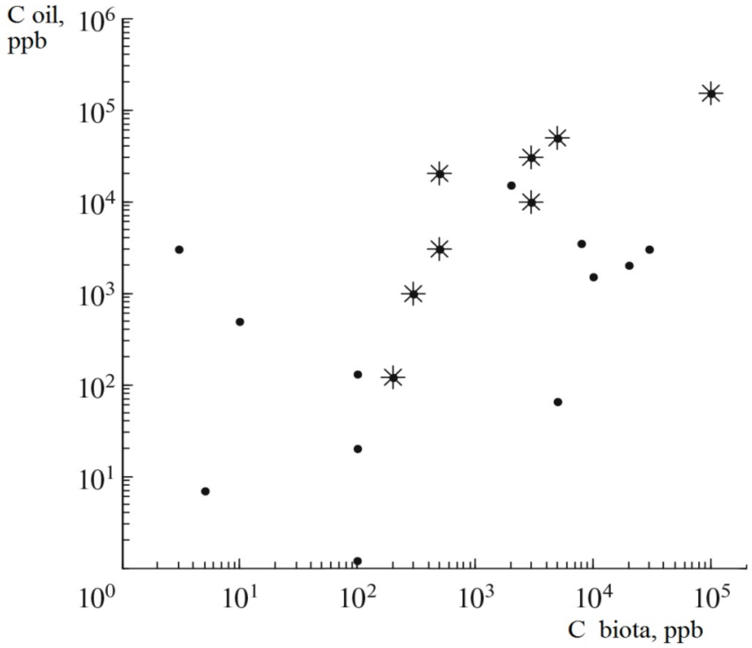


*Figure 2.* Correlation between average trace element concentrations in oil and in living organisms; the "biogenic elements" are denoted by stars

The results presented in Table 1 indicate a stronger correlation between the TE composition of clays, coals, oil shales (all substances of Upper crustal origin) with the chemical content of the upper continental crust (see list of data in (Rodkin et al., 2016)). In contrast, the TE composition of oils tends to correlate closely with the chemical content of the Lower continental crust. It should be noted also that the correlations typical of oils are essentially weaker than those typical of clays, coals, and shales. This indicates a more complex and multifactor character of the formation of oils. The results of the correlation clearly show that the deep crustal factors play a considerable role in the genesis of hydrocarbons and that the process of oil generation is more complex than that of the generation of coals and oil shales. Moreover, sometimes, it seems possible to indicate what type of biota (aquatic or terrestrial, plants or animals) predominates in the process of oil formation.

*Table 1.* Correlation coefficients between logarithms of trace element compositions of clays, shales and mean oil with the different strata of the continental crust and the different types of biota

| | Clays | Coals | Oil shale | Black shale | Mean oil |
|---|---|---|---|---|---|
| Cont. crust | | | | | |
| Upper | 0.90 | 0.84 | 0.84 | 0.82 | 0.60 |
| Middle | 0.85 | 0.76 | 0.76 | 0.84 | 0.58 |
| Lower | 0.84 | 0.78 | 0.79 | 0.80 | 0.63 |
| Types of biota | | | | | |
| aquatic plants | 0.77 | 0.78 | 0.76 | 0.78 | 0.61 |
| terrestrial plants | 0.72 | 0.71 | 0.74 | 0.75 | 0.58 |
| aquatic animals | 0.53 | 0.48 | 0.54 | 0.57 | 0.59 |
| terrestrial animals | 0.46 | 0.50 | 0.55 | 0.56 | 0.54 |

The results of the analysis based upon regional-scale data are presented in Table 2 where data on the various oil-and-gas bearing basins are presented. As can be seen from the table, for oils of all main oil-and-gas bearing basins of Russia the correlation with the Lower continental crust is higher than with the Upper and the Middle crust. However, this is not a general rule. We have found at least two exceptions: for the Kamchatka region both for small oil fields and for oil seeps in caldera Uzon volcano (Dobretsov et al., 2015; Varfolomeev, 2013), and for the huge White Tiger oil field in Vietnam (Punanova, 2004; Punanova et al., 2018). The caldera Uzon volcano is located in the main volcanic chain in Kamchatka, Fig. 3. For these two cases, the correlation with the chemical content of the Upper crust is similar or even higher than with the Lower crust. Besides, in these cases, the correlation with biota is essentially higher than for the main oil-and-gas bearing basins in Russia (Table 2). The possible interpretation of these findings will be discussed below. Concerning the White Tiger huge oil field, it should be noted also that the TE characteristics of oil from the sedimentary strata and from the crustal foundation were found to be close. It supports the idea that the source of oil was common; however, the correlation of TE content of oils from sedimentary layers with biota is slightly higher (Table 2). Note that both mentioned cases of Kamchatka and the White Tiger oil field in Vietnam are located near the current or recent subduction zones.

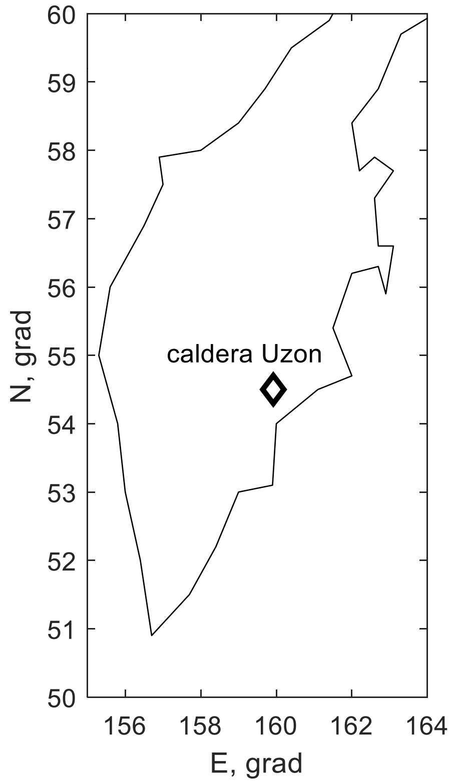


*Figure 3.* Location caldera Uzon with seeps of young oil in Kamchatka

Note also, that sometimes the coefficients of correlation with different types of biota permit to suggest aquatic or terrestrial plants and aquatic or terrestrial animals have dominated as a source of an organic matter in the process of oil generation.

*Table 2.* Correlation coefficients between TE composition of different oils and the chemical composition of the Earth's crust and the types of biota

| Region | Continental Earth Crust | | | Biota | | | |
|---|---|---|---|---|---|---|---|
| | Upper | Middle | Lower | aquatic plants | terrestrial plants | aquatic animals | terrestrial animals |
| Different oil-bearing basins, mean data from (Gottikh, Pisotskii, 2010) | | | | | | | |
| Dnipro-Donetsk | 0.54 | 0.51 | 0.58 | 0.45 | 0.37 | 0.54 | 0.37 |
| Timano-Pechorsky | 0.57 | 0.55 | 0.62 | 0.57 | 0.57 | 0.53 | 0.50 |
| Volga-Ural | 0.59 | 0.60 | 0.63 | 0.54 | 0.60 | 0.61 | 0.52 |
| Western Siberia | 0.69 | 0.68 | 0.73 | 0.71 | 0.73 | 0.60 | 0.65 |
| Eastern Siberia | 0.57 | 0.54 | 0.60 | 0.57 | 0.54 | 0.55 | 0.54 |
| Kamchatka, caldera Uzon, data from (Dobretsov et al., 2015) | | | | | | | |
| Data 2011 year | 0.64 | 0.60 | 0.64 | 0.78 | 0.74 | 0.70 | 0.78 |
| Data 2012 year | 0.64 | 0.60 | 0.65 | 0.74 | 0.69 | 0.67 | 0.76 |
| (Varfolomeev, 2015) | 0.73 | 0.73 | 0.72 | 0.75 | 0.68 | 0.60 | 0.67 |
| White Tiger oil field, from (Punanova, 2004; Punanova et al., 2018) | | | | | | | |
| Lower Oligocene | 0.58 | 0.54 | 0.56 | 0.80 | 0.86 | 0.83 | 0.92 |
| Crystal foundation | 0.58 | 0.54 | 0.56 | 0.76 | 0.84 | 0.80 | 0.91 |

## 4. Discussions

The obtained results can be explained within the scheme of oil-genesis as a flow-through non-equilibrium reactor (Rodkin, 2004; Rodkin, Rukavishnikova, 2015). According to this model, the buried organic matter is the main source of oils, but for a mass oil generation the sedimentary strata should be concentrated and reworked out by an upward water flow of low mineralization. This flow introduces the heat energy and the deep crust components and takes away the oil components that cannot exist a long time at the high-temperature conditions inherent to the deep strata of the Earth's crust. This fluid flow bears the mark of TE concentration characterizing the depth of its formation (Rodkin and Rukavishnikova, 2015; Punanova and Rodkin, 2018).

Thus, according to the (Rodkin and Rukavishnikova, 2015; Rodkin et al., 2016; Punanova and Rodkin, 2018; Punanova and Rodkin, 2019), the TE content of oils has two main sources - an organic matter and a deep crust source which resulted from the uprising deep fluid flow. The contribution of these two sources can change in different cases. Such a suggestion was confirmed below by the examination of the regression between the maximum correlation R-value with an organic matter (Rmax biota) and the difference between the correlation coefficients with the Lower and the Upper crust (ΔR, Lower-Upper crust). The evident connection between these two parameters can be seen in Fig. 4. Similar regression is typical when we have the situation of mixing from two sources. Thus, it can be suggested that we have a mixing of the deep crust end member and the subsurface organic matter end member. The subsurface end member is characterized by a higher correlation with the chemical content of biota and the Upper crust. The deep end member is characterized by the weaker correlation with biota and higher correlation with the Lower crust.

The typical oils of the richest oil-and-gas bearing basins of Russia (Dnipro-Donetsk, Timano-Pechorsky, Volga-Ural, West, and East Siberia) are closer to the deep crust end member, while the young oils from the Kamchatka Peninsula and from the huge White Tiger oil field are closer to the subsurface end member.

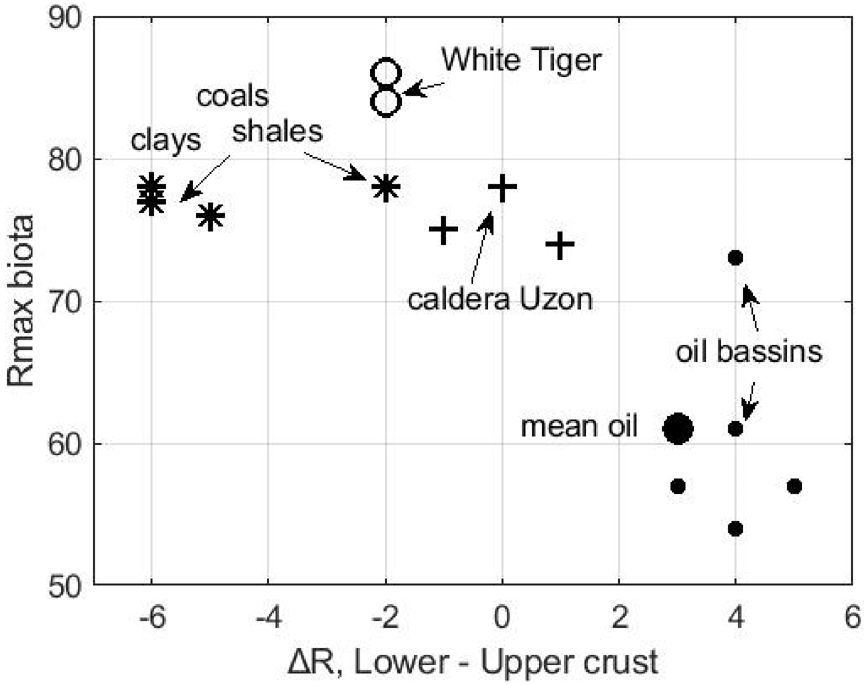


*Figure 4*. The interrelation between the maximum correlations of TE content of different caustobiolites with biota and the difference in their correlation with the Lower and Upper crust. The points corresponding to different oils and other caustobiolites are indicated

The difference between the TE content of oils and the deep waters in Kamchatka and the TE content of oils of the main oil-bearing basins of Russia can be explained easily in terms of the scheme of oil-genesis as a flow-through non-equilibrium reactor (Rodkin and Rukavishnikova, 2015; Punanova and Rodkin, 2018). Under essentially higher deep temperatures in the Earth's crust of Kamchatka, dehydration processes occur here at shallower depths, from here the uprising fluid flow brings trace chemical content of shallow strata of the crust, which explains the difference in the character of the correlation.

The same explanation appears to be available for the case of the White Tiger oil field. This field is located on the oceanic crust with essentially higher deep temperatures than in the typical intracontinental oil-and-gas bearing basins. Besides, the location of the White Tiger oil field appears to be adjacent to the ancient subduction zone. We should note, however, that a number of chemical elements used for the calculation in the case of the White Tiger oil field are essentially less than in the other cases discussed above; in the majority of the cases, we have 35-50 elements and only 10 in the case of White Tiger oil field. Thus, the results obtained for the huge White Tiger oil field need confirmation.

In the interpretation of the presented results, it should be taken into account, however, that an interaction of the ascending fluid flow and hydrocarbon components with the lower crustal rocks occurs at higher temperatures than their interaction with the upper crustal rock. This difference can cause stronger interaction and a closer correlation between the TE composition of oils and the lower crust rock content compared with the upper crustal rock.

The results of this study confirm the effectiveness of a simple technique employed for estimating the degree of correlation between TE compositions of different geochemical reservoirs: oils, coals, shales, organic matter, and different horizons of the continental crust. These results provide additional support for the polygenic model of TE content in oils and possibly of polygenesis of the process of generation of hydrocarbons. In contrast to methods employed by other researchers, the calculation of correlations gives the possibility to quantify the contributions of different sources.

Note, that conclusions on the predominance of TE inputs from different geo-reservoirs (the Upper, Middle, and the Lower crust, organic matter, etc.) can be obtained using the concentration values of a considerably less number of characteristic elements. For this purpose, the so-called characteristic elements may be used. It could be the so-called "biogenic" elements (as it is shown in Fig. 2) or elements mostly specific to the Upper or the Lower crust. Such elements as V, Ni, Fe, Co, Cr, Zn, As, Pb, Au, and B can be used as characteristic biogenic elements. For distinguishing between the predominance of involvement of the upper vs the lower crustal rocks, such elements as Cs, Rb, K, U, V, Cr, and Ni can be used. It was shown (Rodkin et al., 2016), that the composition of samples in terms of characteristic elements exhibits a stronger contrasting correlation with the Upper or the Lower crust, as opposed to the entire suite of all available elements. The use of the characteristic elements only may provide comparable results on the predominance of inputs from different geo reservoirs with a 3-5-fold or greater decrease in the amount of the needed analytical measurements. However, the use of data on the concentration of a greater number of elements seems preferable, because of better robustness of the results obtained.

The evidence of the strong involvement of the lower crustal fluid and matter in the process of hydrocarbon generation testifies in support of the deep fluid circulation through the Earth's crust and in the possibility of high permeability values in the Middle and the Lower continental crust. Note that very high temporal increases in permeability values were found in (Rodkin and Tikhonov, 2016) to be typical of the process of generation of major earthquakes.

## 5. Conclusions

The correlations of trace element (TE) composition in different oils and in different rock types are examined and compared. The strong correlation of TE concentration in the majority of oils with the mean composition of the Lower crust is shown to be typical. This result testifies to the involvement of the deep crust rock and/or the deep fluids in the formation of TE content in oils. This feature of the character of correlation of TE content of oils from different regions is explained in terms of the model of reworking of the organic matter in sedimentary strata by the uprising fluid flow that originates from the dehydration reactions occurring in the Middle and the Lower continental crust at different depths depending on the deep temperature regime. The comparison of correlations of TE content in different oils and other caustobiolites testify to their formation from different sources. The main trend can be interpreted as a model of mixing of two sources, where one source or end member has a high correlation with biota and with the chemical content of the Upper crust, and the second end member has a high correlation with the Lower crust and essentially weaker correlation with biota.

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