Additional factor of organic matter maturation in faulted areas

Sergey M. Astakhov* (Kontiki-Exploration) and Douglas W. Waples (Sirius Exploration Geochemistry)

Abstract

The additional factor of organic matter maturation is presented in terms of mechanical activation. The kinetic model of the vitrinite maturation in faulted, tectonized areas with seismic activity influence is presented. A quantitative assessment of this factor's influence on the chemical reactions of thermal and mechanical organic matter conversion is obtained by using a geomechanically based paleostructural reconstruction. The use of the proposed scheme is reasonable in areas of the direct proximity (20-30 km, up to 50 km) to orogenic structures, foldbelts, in areas of complex tectonics and is expected to be beneficial for exploration.

Introduction

Modeling of the thermal maturation of sediments and organic matter is a key tool in evaluating a source rock's effectiveness. The closer a model approximates the behavior of natural systems, the more confidence we will have in its predictions. The effects of time and temperature on organic maturation are quite well understood, accepted by virtually everyone, and widely used. In contrast, any possible role of mechanical influences, including stress and pressure, in hydrocarbon generation and organic maturation has been widely discounted and ignored in the West. In the USSR, and later in Russia and China, in contrast, considerable research has been carried out that indicates a potentially significant role for mechanical forces in areas where such forces are large. The essential and well-known fact that motivates us is that vitrinite reflectance (VR) increases in faulted and tectonized areas (Cook et al., 1972; Hower and Davis, 1981; Bustin et al., 1986; Levine and Davis, 1989; Langenburg and Kalkreuth, 1991; Littke et al., 2012). It has become clear to some investigators that in such areas other factors, in addition to the generally acknowledged influences of time and temperature, play a role in the thermal maturation of organic matter. Attempts have been made to perform coal and kerogen conversion experiments in a laboratory under conditions close to those that were experienced under geological conditions by applying various physical fields, primarily elastic deformation (Molchanov et al., 1975; Chersky et al., 1985; Petzoukha et al., 1992). Those experiments have led to development of the theoretical foundation of seismicity and tectonic stress as factors in the transformation of organic matter. These two phenomena were combined in the term "dynamocatagenesis", which has become a standard term in the Russian-speaking geological community.

Theory

Among the main causes for the long-running disputes about the role of pressure in coalification are unclear usage of terms, and confusion about the different types of pressure (Cao et al., 2007). In the context of this paper, "fluid pressure" is isotropic pressure exerted on fluids and solids by the fluid. "Normal pressure" refers to fluid pressure that is hydrostatic. The weight of the mineral column is borne by the mineral grains, which include kerogen. This weight provides the most-common form of "grain pressure". Grain pressure normally acts along the z-axis, in response to the force of gravity. However, in areas with stress along the x-axis and/or y-axis, grain pressure must be assumed to be non-isotropic and triaxial.

An additional possible source for both fluid pressure and grain pressure is tectonic compression. If sufficient interconnected tectonic fractures don't develop during tectonic compression, pore fluids will become overpressured. Simultaneously, grain pressures will generally increase, particularly along the x- and y-axes.

Empirical evidence appears to strongly support the idea that fluid pressures above normal hydrostatic pressure lead to retardation of organic transformations. For example, Carr (1999) described a large number of early studies that found empirical correlations between fluid overpressuring and retardation of both VR increase and hydrocarbon generation. It is very important to understand that an empirical correlation between high fluid pressure and retardation of organic transformations might be caused by one or both of two quite different factors. Many authors (e.g., Carr, 1999) have suggested that a buildup of reaction products should, following Le Chatelier's principle, retard the reaction that produced those products. Conceptually this idea is easy to understand, but it has not yet been demonstrated to actually be a cause of retardation. A second factor is also potentially important, though it has been largely ignored by researchers: the rates of the various organic transformation reactions might depend on the grain pressure exerted on the organic particles. In the absence of tectonic stress, high fluid pressure would lead to lower grain pressure, and thus to retardation. However, separating this effect from that due to the buildup of reaction products has proven difficult. In contrast, where tectonic pressure is present, both fluid and grain pressures could increase. Since higher fluid pressure would lead to retardation, while higher grain pressure would lead to faster organic reactions, the net effect would be difficult to predict.

In comparing maturation of naturally deformed and non-deformed coals, Cao et al. (2007) found that deformed coals contain more methane. The deformed coals also exhibited a number of other anomalous properties, including high concentrations of free radicals and chloroform bitumen, and low aliphatic/aromatic carbon ratios (Cao et al., 2003). These data were interpreted to mean that tectonic stress not only affects physical coalification, but also leads to changes in chemical structure and composition of organic molecules in coal. Therefore, tectonic stress affects not only vitrinite reflectance, but also the entire process of hydrocarbon generation.

The history of experiments studying mechanical activation (dynamocatagenesis) in the former USSR and in the Russian Federation is long, and can be divided into three stages:

1.1970-1990: **Fine grinding** in "planetary mills" (nature analog: intra-fault area and shallow marine dispersed rocks)

Conditions: Pure mechanochemistry activation + 70o C; Strong effect: 2-3-rank increase in coal maturity.

2. 1970-1985: **Elastic oscillations** in "magnetostrictor devices" (nature analog: seismic waves)

Conditions: 1-30Hz, temperature = 20 to 70o C; Medium effect: 1- to 2-rank increase in coal maturity

3. 1980-1990: **Plastic deformation** and fracturing in "triaxial devices" (nature analog: tectonic stress)

Conditions: Triaxial stress: 120 MPa axial, 35 MPa surrounding pressure above 20o C; Medium-low effect: mostly in immature stage (VR<0.5%)

Fine grinding of coals in planetary mills represents the first experiments that had recognized by number of analytical procedures (Molchanov et al., 1975) the mechanochemical effect on the chemical structure of organic matter.

Other laboratory experiments in the USSR proved the possibility of transformation of organic matter and hydrocarbon generation using magnetostrictor oscillations and triaxial stress (Chersky et al., 1985; Petzoukha et al., 1992).

To study plastic deformation and its influence on the evolution of organic matter in source rock, Petzoukha et al. (1992) carried out a deformation experiment at room temperature (20^{o}C) using modern calcareous clay sediments of Karachy Lake in Western Siberia. The samples contained 3.7 % TOC consisting of Type II kerogen. Prior to deformation, standard samples were created by extraction and drying. These standard samples were then subjected to a pressure of 35 MPa isotropic surrounding pressure and 120 MPa uniaxial pressure for 3 hours, without heating.

The results indicated that after deformation the pyrolysis S2 peak increased. In addition, the quantity of free lipids increased by a factor of four; the hydrocarbon proportion in the free lipids increased by a factor of 12; the concentrations of steranes and hopanes increased; and the sterane distributions took on a more-mature look. Because these experiments were carried out at room temperature, where hydrocarbon generation would not be expected to occur, the observed increases in hydrocarbons confirms that mechanical energy alone is capable of bringing about the chemical transformation of organic matter. The authors noted that variable levels of tectonic stress during deformation resulted in structural changes in the kerogen. In their interpretation, these structural changes led to a decrease in the activation energies of the bonds that were broken in the transformation processes. After deformation, the modal value in the distribution moved from 55 kcal/mol to 49 kcal/mol (Fig. 1).

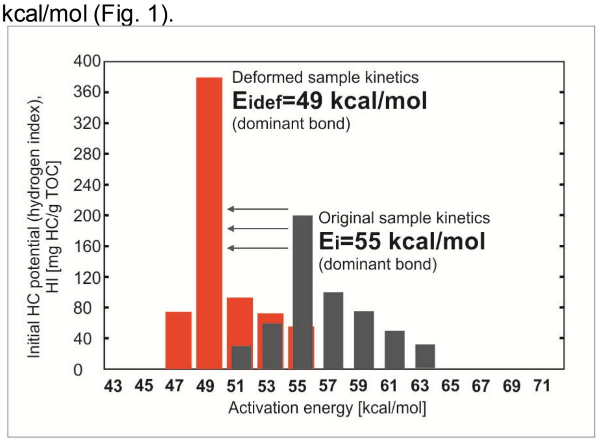

Figure 1. Decrease in activation energy obtained from experiments by Petzoukha et al. (1992). Grey distribution was calculated from pyrolysis data obtained from an original (non-deformed) sample. Red distribution was obtained by the same pyrolysis process from the same sample after it was subjected to differential confining pressure but no heating. The A factor is the same for both distributions.

They also noted an increase in total hydrocarbon yield during generation from the deformed samples. This increase in quantity is shown in Figure 1 by the increase in the total yield after deformation (sum of the contributions from the red histogram, compared to those from the grey histogram).

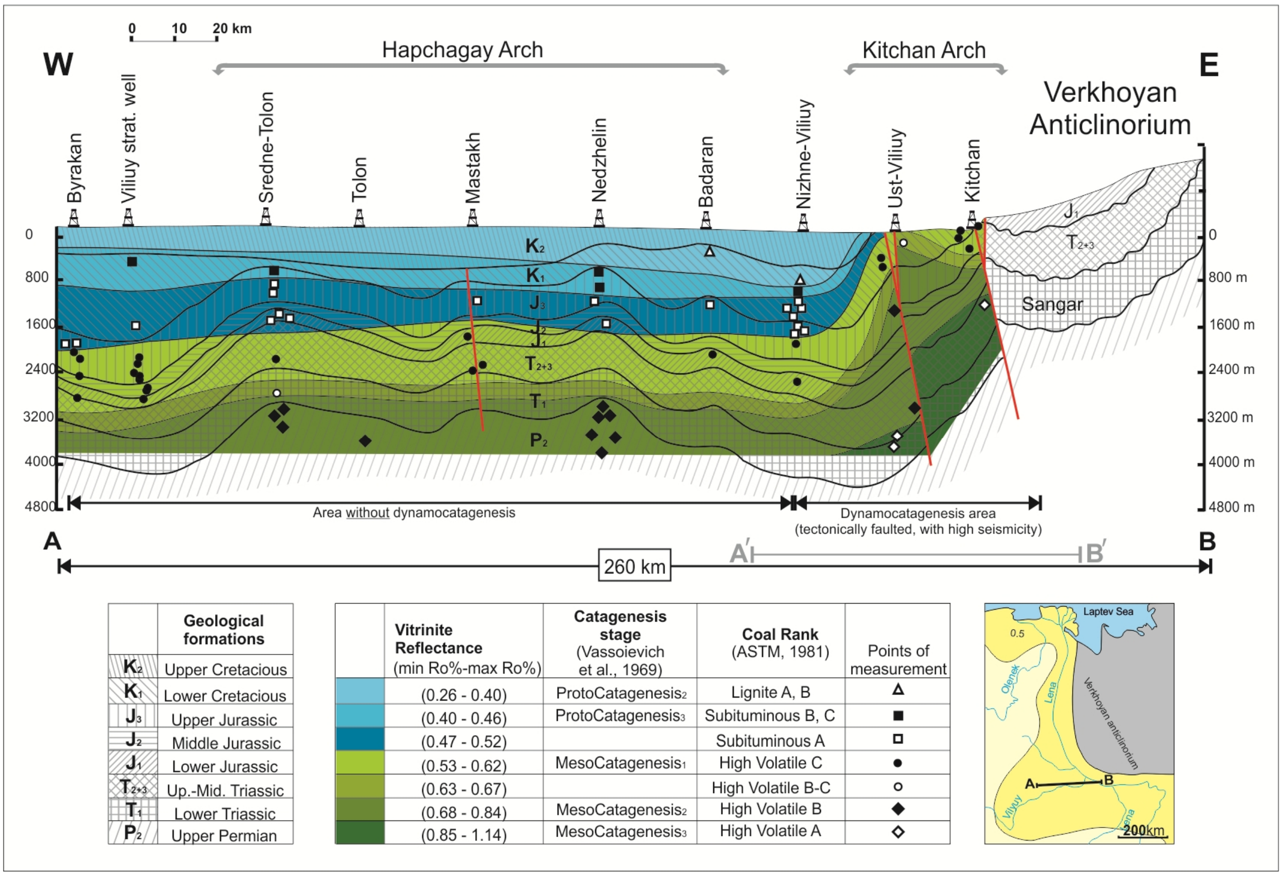

Figure 2. Geological structure and present-day catagenesis zones (thermal maturation as expressed in terms of vitrinite reflectance and coal rank) within the Vilyui and Priverkhoyan basins. The location of the section is indicated on a regional sketch map of the northern Vilyui basin and Priverkhoyan foreland (inset). Colored vitrinite-reflectance intervals in the legend correspond to the catagenesis stages (Vassoievich, 1986) and coal ranks (ASTM, 1981).

Other experimental data suggest that mechanical energy plays a role in the elimination of hydroxyl and carboxyl groups during maturation of coal and kerogen from “High volatile B” to “High volatile A” rank (Chersky et al., 1985). This transformation was achieved after application of magnetostrictor waves (30 Hz) with simultaneous heating to 70 ^{o}C. No transformation was achieved with lower-energy waves (1Hz) with the same amount of heating. Structural changes in the kerogen were also documented: a "decrease in C-O groups, reducing the intensity of the aliphatic C-H bonds, with a simultaneous increase in the intensity of bands due to the presence of differently-substituted aromatic compounds and condensed aromatics".

The fundamental physical explanation of dynamocatagenesis comes from mechanochemistry theory (Baramboim, 1971). The principal mechanism that drives dynamocatagenesis is thus called “mechanochemical” and bases on the decreasing of activation energies after mechanical forces application.

Examples

Biaxial coal and vitrinite reflectance ellipsoides were used in several studies to explain the different coalification in the presence of directed stress (Cook et al., 1972; Hower and Davis, 1981; Bustin et al., 1986; Kilby, 1988; Levine and Davis, 1989; Langenberg and Kalkreuth, 1991). This well known vitrinite reflectance anisotropy of deformed coals is interpreted from the ordering degree promoted by the stress and caused by the macro-molecular directional hyperplasia. It was recognized by Cao et al (2007). For example, Littke et al. showed that vitrinites in different microtectonic domains (cleavage domains) in the Devonian rocks of Rursee area (northern Rhenish Massif, Germany) revealed significant differences in both maximum vitrinite reflectance and vitrinite reflectance anisotropy (Littke et al., 2012).

There are many examples with vitrinite reflectance increased locally in folds and faulted zones in Post Soviet territory without additional hydrothermal/convection or uplift/erosion factors. The section (Figure 4) along the Vilyui syneclise and Priverkhoyan foreland, where dynamocatagenesis is developed locally (Chersky et al., 1985) is presented at figure 2.

Let us state key conditions of the study:

1.Temperature is the main factor of the organic matter maturation;

2.The mechanical factor of organic matter maturation (dynamocatagenesis) influences the sediments in stressed areas;

3.The percent of heat that develops from the mechanical energy is negligible for modeling;

4.Mechanical energy reduces the bond rupture activation energies in organic matter molecules.

The quantitative characteristics of dynamocatagenesis factor are assessed with the assumption that the thermal maturation factor effectiveness has the same value in a stress area between faults. It is clear from the fig. 2 with vitrinite isoreflectance lines: vitrinite reflectance rises near the fault (Ust-Vilyui area), then values decrease eastwards and finally increase again when approaching next fault (Kitchan area).

Results

The standard model suggests that temperature and time are the only factors, that influence the vitrinite reflectance increasing. Here we introduce a stress dependent variable Estress, which can decrease the activation energy according to the fourth key condition of this study and to the theory of mechanochemistry:

$$Ki(t')=A*\exp(-(Ei + Estress) /RT(t')) \qquad (1)$$

Estress – calculated value of the activation energy decrease (for the whole spectrum). Estress has negative values for showing the decreasing of the activation energy of each set of reactions from the standard spectrum proportionally on the calculated value.

Decreasing the activation energy of any chemical reaction increases the rate of that reaction. In the case of reactions involved in Ro change, the higher rates from equation (1) lead to higher calculated Ro values than those calculated using the conventional Easy%Ro model (Sweeney and Burnham, 1990). The most prominent example of dynamocatagenesis of our study is presented in Figure 3 by comparing observed Ro changes in two wells that have experienced different stress regimes. The Nizhne-Viliuy well, which is 15 kilometers from the Ust-Viliuy fault, is considered to be either entirely free of dynamocatagenestic influences, or at least much less affected than the Ust-Viliuy well, which is very close to the deformation (Fig. 3).

The original Ro model shown in Figure 3e was calculated using 2-D basin-modeling software (PetroMod), with the entire transect calibrated to the measured Ro values from the undeformed Nizhne-Viliuy well (Fig. 3d). However, the Ro profile in the undeformed area (Nizhne-Viliuy well) (Fig. 3d) is quite different from that in the deformed zone near the Ust-Viliuy well (Fig. 3e). The difference between the two wells, however, is limited to the upper layers of the Ust-Viliuy well (Fig. 3f), and the difference eventually disappears with increasing depth. The Ro anomaly corresponds in depth to the paleostress anomaly (Fig. 3c). The magnitude of the maximum paleotemperature anomaly also decreases with depth (Fig. 3a).

The last of the dynamocatagenesis episodes took place at the end of the Early Cretaceous. As shown in Figure 3f, Ro in the Lower Cretaceous layer at the Ust-Viliuy well was first calculated, in the absence of dynamocatagenetic effects, as 0.33%. The measured Ro value at that level in that well is actually 0.59% (Fig. 3f). The maximum temperature at the end of the Early Cretaceous in the middle of the Lower Cretaceous layer was calculated to have been 37 ^{o}C. We used this temperature regime and the assumption that the dynamocatagenetic effects lasted for one million years to determine empirically that the value of Estress required to fit the measured Ro trend in Figure 3f is **- 5 kcal/mol** for the faulted area near Ust-Viliuy fault of the Priverkhoyan foreland.

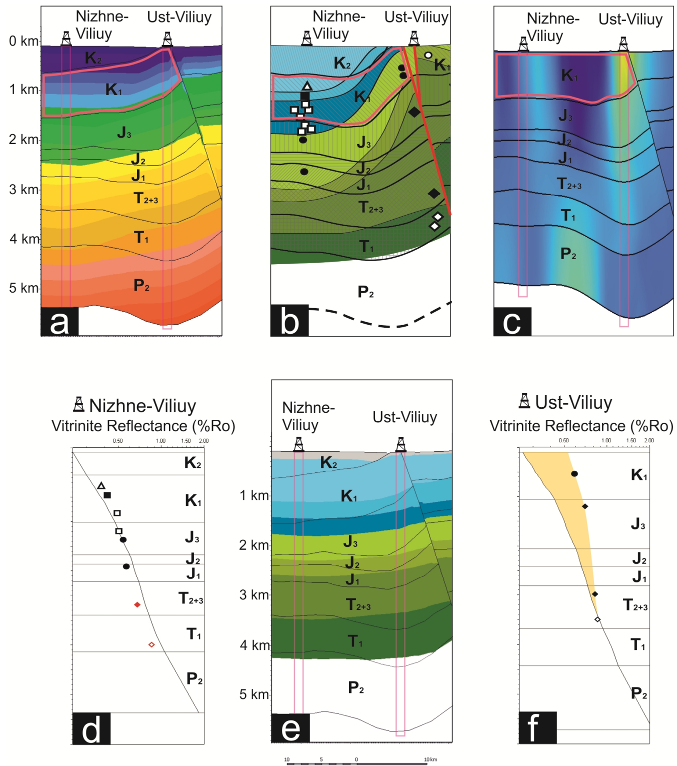

Figure 3. Plots showing calculated and measured present-day maturity trends at the Nizhne-Viliuy and Ust-Viliuy wells, as well as present-day maturity trends along the section that connects those two wells. (a); Maximum paleotemperatures; (b): Present-day Ro values using the color scheme from Figure 6; (c): Paleostress parameter using the color scheme from Figure 8, showing an anomaly in the upper layers of the Ust-Viliuy well (yellow-colors); (d): Present-day calculated Ro profile for the Nizhne Viliuy well, together with measured Ro data; (e): Calculated present-day Ro regime calibrated using the measured Ro data from the Nizhne-Viliuy well; (f): Present-day Ro profile calculated without considering dynamocatagenesis effects (black line), compared to measured Ro data in the Ust-Viliuy well. The beige color field shows the magnitude of the Ro anomaly.

The dark grey bands of Fig. 4 show the organic matter transformation reactions with dynamocatagenesis at its maximum in the close proximity to the fault. Decrease in activation energy should increase vitrinite reflectance from 0.33% “Lignite B” to 0.59% “High volatile C bituminous”. In other words the reactions to achieve

VR=0.59% (with temperature = 37 °C and duration of dynamocatagenesis process of 1 million years) will take place only under the condition of decreasing the spectra of activation energies by 5 kcal/mol.

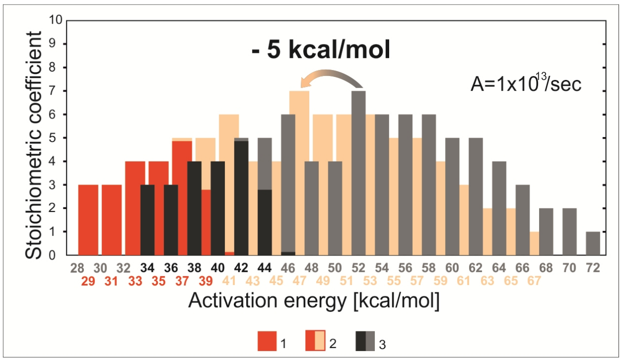

Figure 4. Activation energy decrease as a result of dynamocatagenesis. Grey bands represent the Easy % Ro spectra that needs to be artificially reduced in areas with dynamocatagenesis. Such areas can be defined by actual data (measured biaxial vitrinite reflectance) and also be predicted by using geomechanical structural reconstruction. The value the spectra shall be reduced depends on paleostress calculated. Legend: 1 - Calculated kinetics to achieve Ro=0.59% of the vitrinite transformation at temperature = 37 deg. C at the end of Early Cretaceous; 2 - The whole EasyRo spectra decreased by Estress = -5kcal/mol; 3 - Standard EasyRo spectra.

Conclusions

This scheme allows the combination of geomechanical reconstructions and kinetic calculations. It represents a tool for modeling the dynamocatagenesis intensity using the equations that exist in petroleum system modeling software.

Two conclusions can be drawn:

1. A theoretical model of the impact of mechanical energy on kinetics of the hydrocarbons formation process is developed. It is based on observations of the degree of vitrinite reflectance in tectonically stressed areas. The model is supported by data and an example of application of the proposed technique in Priverkhoyan and Vilyui basins.

2. The use of the proposed model is reasonable in areas of direct proximity (20-30 km, up to 50 km) to orogenic structures and foldbelts in areas of complex tectonics. The use of an additional mechanism of mechanochemical reactions in VR evaluation for large sedimentary basins with low tectonic activity is not required. It is so, because thermal maturation in unstressed basins runs under the "normal laws" that are well understood.

Currently, the hydrocarbon generation modeling in a basin and petroleum system modeling software is based on kinetics, calculated from the results of the pyrolysis of source rock samples in different basins. Now it is recommended to use the edited kinetics in compressional basins, by excluding Estress, which is determined from the results of the geomechanical reconstruction. Earlier matured source rocks generate and expel oil and gas faster. In such circumstances the whole process of migration and accumulation will go another way more or less. That is the reason why the picture of prospects will change in exploring basin. Basins without significant sedimentary cover (less than 2 km) but with mechanical energy sources will be under hot conditions in these circumstances. However, a lot of work by joint efforts of various research teams from different countries is called to adjust the proposed model.

Acknowledgments

We thank Prof. Dr. Anatoly Reznikov for his enthusiastic support, and Prof. Dr. Anatoly Bochkarev and Prof. Dr. Nikolay Lopatin for helpful advice during the execution of this study.

References

ASTM, 1981. Standard specification for classification of coals by rank; Standard D388-77. In: 1981 Annual Book of ASTM Standards, Part 26, Gaseous Fuels, Coal and Coke, Atmospheric Analysis, p. 214-218.

Baramboim, N.K., 1971, Mechanochemistry of polymers, Chimiya, Moscow, 261 p. (in Russian)

Bustin, R.M., J.V. Ross, and I. Moffat, 1986, Vitrinite anisotropy under differential stress and high pressure and temperature: preliminary observations, International Journal of Coal Geology, v. 6, no. 4, p. 343-351

Cao, D., X. Li, and S. Zhang, 2007, Influence of tectonic stress on coalification: Stress degradation mechanism and stress polycondensation mechanism, Science in China. Series D: Earth Sciences, v. 50, no. 1, p. 43-54.

Cao, Y., A. Davis, R. Liu, X. Liu, Y. Zhang, 2003, The influence of tectonic deformation on some geochemical properties of coals: a possible indicator of outburst potential. International Journal of Coal Geology, v. 53, no. 2, p. 69-79.

Carr, A.D., 1999, A vitrinite reflectance kinetic model incorporating overpressure retardation: Marine and Petroleum Geology, v. 16, p. 355-377.

Chersky N.V.,V.P. Tsariov, T.I. Soroko, and O.L. Kuznetsov, 1985, Influence of seismic and tectonic processes on the formation and accumulation of hydrocarbons, Novosibirsk, Nauka, 224 p.(in Russian).

Cook A.C., D.G. Murchison, and E. Scott, 1972, Optically biaxial anthracitic vitrinites, Fuel, v. 51, p. 180-184.

Hower, J.C. and A. Davis, 1981, Vitrinite reflectance anisotropy as a tectonic fabric element, Geology, v. 9, p. 165-168.

Kilby, W.E., 1988, Recognition of vitrinite with non-uniaxial negative reflectance characteristics, International Journal of Coal Geology, v. 9, no. 3, p. 267-285.

Langenberg, W. and W. Kalkreuth, 1991, Tectonic controls on regional coalification and vitrinite anisotropy of Lower Cretaceous coals in the Alberta Foothills, Canada, Bulletin de la Société géologique de France, v. 162, p. 375-383.

Levine, J.R. and A. Davis, 1989, The relationship of optical fabrics to Alleghanian tectonic deformation in the central Appalachian fold-and-thrust belt, Pennsylvania: GSA Bulletin, v. 101, p. 1333-1347.

Littke, R., J.L. Urai, A.K. Uffmann, and F. Risvanis, 2012, Reflectance of dispersed vitrinite in Palaeozoic rocks with and without cleavage. Implications for burial and thermal history modeling in the Devonian of Rursee area, northern Rhenish Massif, Germany, International Journal of Coal Geology, v. 89, p. 41–50, doi: 10.1016/j.coal.2011.07.006.

Molchanov, V.I., A.A. Gontsov, and T.A. Andreeva, 1975, Experimental study on conversion of organic humic substances in a hydrogen generation conditions after mechanical activation, In Physico-chemical studies of mechanically activated minerals, Novosibirsk, IGiG the Academy of Sciences of the USSR, p. 125-149 (in Russian).

Petzoukha, Yu., O. Selivanov, V. Bourkova, A. Fomin, and N. Vorobjova, 1992, A new approach to source rock transformation on exposure to differential confining pressure, In 13th World Petroleum Congress Proceedings (Buenos Aires, Argentina), p. 203-213.

Sweeney, J.J. and A.K. Burnham , 1990, Evaluation of a simple model of vitrinite reflectance based on chemical kinetics, AAPG Bulletin, v.74, no. 10, p. 1559-1570.

Vassoievich, N.B., 1986, Selected works. Geochemistry of organic matter and the origin of oil, Moscow, Nauka, 368 p.(in Russian).