Thermodynamic simulation of the interaction of the system "water - mineral sediment - organic matter" at the diagenesis stage

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Abstract. The current study examines thermodynamic calculations of interaction of the "water - mineral sediment - organic matter" system at temperatures and pressures of diagenesis. In the course of reactions mature kerogen forms in the system, mainly C292H288O12, rarely C128H68O7 including accompanying substances (hydrocarbons, nitrogen compounds). The removal of CO2 (g) and N2 (g) from the system promotes the reaction. It is found that the aqueous phase during the formation of kerogen does not change significantly. In general, there occur desalination and changes of pH and Eh, as well as the increase in dissolved CO2 content in water composition.

1. Introduction

Diagenesis is termed as a process, where the system is close to equilibrium in condition of a shallow burial and which leads to consolidation of the sediment. At the stage of subaqueous diagenesis, first of all, biogenic residues and rocks that differ in mineralogical composition accumulate at the bottom of ponds.

The analysis of materials showed that the first stages of transgressions and regressions [12] provide the most favorable conditions for the accumulation of organic matter (OM). They usually require a number of conditions: shallow water, accumulation of fine-grained material, active inflow of autochthonous and allochthonous organic matter, alternation of sea and freshwater facies. The continental slopes are regarded as another type of environment that is favorable for organic matter accumulation. They are characterized by normal sea conditions, i.e. high primary productivity of the coastal waters, as well as the inflow of materials formed on land (Figure 1). Here, as a rule, the optimum ratio between the rate of sedimentation and the dynamics of the water masses is maintained, which, in its turn, stipulates precipitation with a high content of OM. According to Tissot and Welte [7], water salinity has no direct effect on organic matter accumulation, but it largely depends on the bioproductivity of water. For high levels of biological productivity, the presence of nutrients (phosphate and nitrate), light, temperature typical for continental margins is of great importance. For preservation of organic matter on the bottom of the water body, clayey fine-grained sediment characterized by limited access of oxygen is the most favorable. The adsorption of the dissolved OM on the surface of the mineral particles increases its stability, since such an OM is more protected from the attack of bacteria and it quickly dips through the water column [7]. However, the accumulation of dissolved OM is of secondary importance from the viewpoint of petroleum formation, in comparison...
with the accumulation of detrital material, because the water-insoluble compounds are the main material for the formation of hydrocarbons (HC).

During silt deposition, the system enters the stage of diagenesis. Freshly deposited sediments have high moisture and high porosity. Their moisture content may reach 86-96% according to [8]. When sediments go deeper, water column and organic matter deposited on the subsequent stages of sedimentation exert pressure on the buried sediments. With increasing pressure, porosity reduces and water is squeezed out from clays. In the process of diagenesis, some components of sediments dissolve, and authigenic minerals form. At the final stage of diagenesis loose sediments become a sedimentary rock.

![Figure 1. Schematic diagram showing environments of deposition.](image)

2. Simulation scheme

Based on the geological conditions, the task is to model the interaction of the system components "mineral sediment - organic matter - pore water" under the condition of changing temperature and pressure. The chemical composition of three types of living matter, i.e. algae, zooplankton, and green plants, the organic matter are analyzed in the current study (Table 1).

| Elements | Algae, planktonic algae | Bacteria | Plants | Biosphere |
|----------|-------------------------|----------|--------|-----------|
|          | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 4 |
| C        | 39.1 | 34.5 | 48.2 | 56.4 | 54.0 | 52.4 | 45.2 | 45.4 | 50.0 | 18.0 |
| H        | 4.6 | 4.1 | 7.7 | 4.8 | 7.4 | 7.9 | 6.2 | 5.5 | 6.1 | 10.5 |
| O        | 53.2 | 47.0 | 36.9 | 27.4 | 23.0 | 28.0 | 46.7 | 41.0 | 42.5 | 70.0 |
| N        | 1.7 | 1.5 | 7.2 | 11.4 | 9.6 | 11.7 | 1.9 | 3.0 | 0.2 | 0.3 |
| S        | – | 1.2 | – | – | 0.53 | – | – | 0.34 | – | 0.05 |

The atomic ratio in living matter

|          | H/C | O/C |
|----------|-----|-----|
| Algae    | 1.42 | 1.63 |
| Bacteria | 1.02 | 0.32 |
| Plants   | 1.44 | 0.77 |

Note: 1 - authors' estimates; 2 - Ermakov, 2008; 3 - Kholodov, 2006; 4 - Vinogradov, 1954 [2]
The elemental composition of living matter is taken from [8] and [3]. For comparison, it was calculated on the basis of the chemical composition and the ratio of the mass of organic matter of the diagenesis main products. In our opinion, the data provided by V.V. Ermakov are more justified. According to the research literature, mineral sediments are mainly composed of clay (75%) and carbonate (25%) material. The chemical composition of the mineral component is taken from [5]. The chemical composition of the water is taken as a standard composition of seawater SW0 [4].

Based on thermodynamic simulation programs [1, 9], it is possible to simulate chemical reactions if the Gibbs free energy of the participants of the reactions and their masses are known. One of the solids that forms during the process is kerogen. Its free energy that can be of five types is shown in Table 2. These five types represented by Helgeson are reference models of kerogen, which correspond to the natural samples. Kerogen of C\textsubscript{515}H\textsubscript{506}O\textsubscript{72} composition is an organic matter that has not yet passed the stage of diagenesis. Other types contain fewer amounts of simple and mixed ethers, they do not contain alcohol groups which are abundantly present in the immature kerogen of C\textsubscript{515}H\textsubscript{506}O\textsubscript{72} composition. Diagenetic process causes deoxygenation of immature kerogen characterized by lower O/C ratios. The maturation is accompanied by the formation of aromatic groups. Among the discussed types, kerogen of C\textsubscript{128}H\textsubscript{68}O\textsubscript{7} composition is considered mature.

Thermodynamic properties of hydrocarbons are taken from [11].

| H/C | O/C | Formula | \(\Delta fG^\circ\) | \(\Delta fH^\circ\) | S\(^\circ\) | V\(^\circ\) | C\(_p^\circ\) | C\(_p^\circ\)=a+bT+cT\(^2\) |
|-----|-----|---------|---------------------|---------------------|----------|----------|-----------|-----------------|
| 1.68 | 0.053 | C\(_{415}\)H\(_{698}\)O\(_{22}\) | 80405 | -2865436 | 2128.66 | 5654.1 | 2079.97 | -2007.70 | 12178.7 | 405.88 |
| 1.30 | 0.047 | C\(_{400}\)H\(_{653}\)O\(_{19}\) | 402917 | -1829146 | 1781.98 | 5086.4 | 1768.93 | -944.01 | 8344.4 | 200.06 |
| 1.16 | 0.14 | C\(_{513}\)H\(_{596}\)O\(_{72}\) | -1248076 | -4123990 | 2133.34 | 6989.3 | 2211.50 | -3577.45 | 16695.7 | 721.04 |
| 0.99 | 0.041 | C\(_{292}\)H\(_{288}\)O\(_{12}\) | 528693 | -684086 | 1124.69 | 3398.2 | 1096.89 | -107.37 | 3930.6 | 28.76 |
| 0.53 | 0.055 | C\(_{128}\)H\(_{68}\)O\(_{7}\) | 358000 | 52282 | 383.77 | 1320.7 | 390.60 | -83.82 | 1539.9 | 13.60 |

Note: \(\Delta fG^\circ\) and \(\Delta fH^\circ\) cal mol\(^{-1}\), S\(^\circ\) and C\(_p^\circ\) cal mol\(^{-1}\) K\(^{-1}\), V\(^\circ\) cm\(^3\) mol\(^{-1}\).

At the first stage of simulation, the system is added by a mixture of moisturized loose deposits composed of organic and mineral sediments. According to the research literature and after conversion to the unit of weight, the system represents a following mixture: 30 kg of “living” matter +14 kg carbonate mineral material + 56 kg of clay mineral material + 4258 kg of sea water. The amount of sea water is calculated based on the original porosity of moisturized silt, which can reach 90% or more. The mass of initial materials contributes to a mass of reaction products, which can be considered in the capacity of 100 kg of bottom silt. At each stage of simulation, the system is exposed to increasing temperature (from 10 to 60 °C, step 1 °) and pressure (from 10 to 135 bar, step 2.5 bar), which corresponds to the temperature and baric conditions of diagenesis. Water is removed from the system in accordance with the data presented in [7, 8]. Thus, the system is exposed to the impact of diagenetic transformations and as a result of calculations the ultimate state of the system is reached. It is due to the fact that calculations are based on an equilibrium approach.

3. Simulation results.
As the result of the calculations, the following mineral products of reaction were obtained: quartz, kaolinite, K, Li-mica, Mg, Ca-dolomite, ankerite, siderite, pyrite, Sr, Ca-calcite. Along with CO\(_2\), CH\(_4\) and homologs, kerogen C\(_{292}\)H\(_{386}\)O\(_{12}\) or kerogen C\(_{128}\)H\(_{68}\)O\(_{7}\) formed; in some cases, both types of kerogen form. In addition to kerogen, the reaction mixture also yields carbon dioxide from hydrocarbons, predominantly methane: as the temperature increases, the concentration of CH\(_4\) (aq) rises (experiments with algae and green plants), or insignificantly varies (zooplankton). At the same
time, the proportion of alkanes in hydrocarbons decreases, while the concentration of CO$_2$ (aq) increases with increasing temperature. [6]. It is known that during sedimentation process sediments emit CO$_2$ (oxidation product of organic matters) and N$_2$ (the product of oxidation of ammonium nitrogen). In corresponding geological literature, there are no quantitative characteristics of the degassing, therefore, there was no possibility to reconstruct cleavage reaction of the living matter. Thus, the removal of gases from the system was made arbitrarily, depending on their amount. The available data on modeling is not enough to make a numerically reasoned judgment, but it is clear that degassing involves acidification of the aqueous phase: removal of CO$_2$ (g) reduces the concentration of bicarbonate and carbonic acid, and removal of N$_2$ (g) reduces the concentration of ammonium nitrogen.

In the course of simulation, sea water changes its pH and Eh values (Figure 2). In addition, the desalination effect is also registered, which corresponds to the data provided in [10]. The chemical composition of water is Cl-HCO$_3$ Na with a very low SO$_4$ content. During the simulation, ionic strength of water reduces from 4 to 2.3 in all systems, regardless of the living matter type, therefore, salinity decreases. In all systems, a high content of ammonium nitrogen is registered in water.

![Figure 2. Changes in aqueous solution pH and Eh during the simulation process in the system with living matter: 1 - algae, 2 - zooplankton 3 - green plants.](image)

### 4. Conclusions

Thermodynamic simulation of the interacting system "living matter - mineral material - standard sea water" was performed at the parameters of diagenesis. In the course of reactions, kerogen and accompanying substances (hydrocarbons, nitrogen compounds) formed in this system. It was shown that the removal of CO$_2$ (g) and N$_2$ (g) from the system stipulates the reaction. In addition, it was revealed that the aqueous phase during the formation of kerogen does not change significantly. In general, desalination, changes of pH and Eh, and increase in dissolved CO$_2$ content in water composition were registered.

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