

Generation of hydrocarbons: Mechanism of reaction, geologic and experimental evidence

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Abstract. A reaction for synthesis of hydrocarbons is considered in terms of a conceptual aqua-complex $[2\text{SiO}_3 - \text{OH}_2 - \text{M}^{n+}2\text{M}^{m+}\text{O}'_4]$ ($n = 1, 2$; $m \geq 3$, O' - volatiles). Structural and chemical rearrangements are catalyzed within clay medium. Catalytic reactions are triggered by energy disequilibria in mineral systems caused by strain from the burial and compaction of sediments and by rock deformations during which C substitutes for Si in argillaceous rocks. Organic matter reduces C, which participates in the synthesis of hydrocarbon products. At present, this reaction is taking place in the bottom sediments of the Solenoe Lake (Kulunda steppe) located within one of several tectonic zones that parallel the main orogenic belt of the Altai. Geologic evidence and results of complex study of the bottom sediments support the relevancy of the proposed reaction mechanism, which combines "organic" and "inorganic" viewpoints on the origin of oil and gas.

Keywords. Hydrocarbons, clay, aqua-complex

1 Introduction

Prospecting for and extraction of oil and gas deposits depend strongly on understanding how the formation of hydrocarbon products occurs in nature. At present, there are two contrary extant concepts of origin of oil and gas. One, the "organic" theory, refers to data from stereochemistry, which implies formation from natural hydrocarbon products including those ones typical of bio-organics and notes that many large deposits are hosted by sedimentary rocks rich in organics. The proponents of the "inorganic" view address to numerous cases of hydrocarbon mineralization in rocks of various kinds and to a lack of balance between the petroleum bodies and the buried fossils.

As discussed at recent conferences, applications from the field of geodynamics may help solve this problem. Geodynamics implies an active role of the mineral continuum in the formation of mineral deposits. Specifically, the accepted theory with its notions of "source", "transport" and "deposition" of metals gives way to an understanding of an active role of the whole mineral continuum whose evolution "works" for concentrating useful elements in deposits, and of the energy aspect of these processes. However, after putting the problem this way we face the question of wondering what specific mechanism guides

the alteration of the rock matter. And does a universal mechanism for various rocks exist? If the Earth can be viewed as a single entity, the answer is likely to be yes.

2 The Aqua-complex approach

The concept of the aqua-complex $[2(\text{Si}, \text{T})\text{O}_3 - \text{OH}_2 - \text{M}^{n+}2\text{M}^{m+}\text{O}'_4]$ (Fig. 1) is based on data obtained from studies of the alteration of minerals in the rocks of gabbro-granite series (Stenina and Distanova 1991). The aqua-complex is composed of three parts: the left part (SiO_2) is acid, the right (MO_2) is basic; the water molecule is presented as a charged tetrahedron built up in the centre, as a redox bridge between both parts. This model is supported by the "quartz" - water structure proposed by Bernal and Fowler (1933). On the basis of our own and published data, the aqua-complex was proposed as a geochemical entity, responsible for: i) the diversity of mineral matter, ii) structural-chemical transformation and redeposition of mineral matter, iii) element associations, iv) formation of granitic melt, v) conversion of energy within the Earth's crust (Stenina 1995).

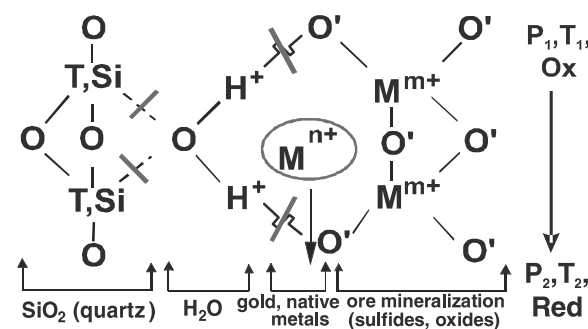


Figure 1: Model for aqua-complex: T - tetravalent ions (C, Sn, Pb, U); M^{n+} - uni and di-valent cations (Na, Au, Cu, Fe^{2+} , etc.); M^{m+} - multivalent ions (Al, Fe^{3+} , As, Mo, etc.); O' - volatiles; --- donor-acceptor, \sim - hydrogen bonds. Combined state as a structural unit of mineral-forming medium and disintegration into quartz-water-ore as a result of redox inversion and/or P, T drops in mineral system.

Table 1: Energies of chemical bonds with oxygen (from Gurvich et al. 1974)

Elements	E (kcal/mol)
C (T)	256,16 ± 0,08
Si	190 ± 2
U	180 ± 4
Al (M ^{m+})	120 ± 3
Fe	97 ± 3
W	160 ± 10
Y	170 ± 3
Nb	180 ± 3
La (REE)	190 ± 10
Cu (M ⁿ⁺)	63 ± 10

In metamorphism, the aqua-complex concept explains the driving forces and mechanisms of mineral replacement. The latter is stimulated by eliminating the excess energy caused by strain in rock deformation and sediment burial-compaction. The aqua-complex possesses a wide range of energies due to varied bond strengths of T and M cations within oxygen polyhedra (Table 1). Energy imbalances in a mineral system are reduced by the extraction from mineral matter of cations with appropriate M (T) — O bond energies and incorporating them into new species. This induces mineral matter to rearrange, and such a process parallels metamorphic replacement. Rock-forming silicates have complex structures with [SiO₄] and [AlO₄] tetrahedra as the major building units. It is unlikely that their transformation goes through complete disintegration and the formation of entirely new phases from separate atoms. The aqua-complex, the smallest unit from which all minerals may be derived, performs structural-chemical rearrangements. In effect, the left part of the aqua-complex corresponds to quartz and other simple oxides; the right side – to complex oxides, sulfides and other salts. Integration of both parts and whole aqua-complexes can yield a great diversity of silicate minerals. Atomic rearrangements in the mineral-forming medium proceed by exchange of chemical bonds, facilitated by water. Generation of hydrocarbons in sedimentary rocks was considered in terms of the aqua-complex concept.

3 Mechanism of reaction of synthesis of hydrocarbon products

In diagenesis, atomic rearrangements in the primary sediments proceed by exchange of chemical bonds facilitated by water. This process stops abruptly when a mineral system suffers drastic fluctuations in pressure, temperature or redox conditions. Under these conditions the weak donor-acceptor and hydrogen bonds, which exist between dipole water molecule and both, left and right radicals are broken,

and the aqua-complexes disintegrate to SiO₂, water and MO₂ (Fig. 1). Ca (Sr, Ba) also play a significant role in destroying aqua-complexes. The structure of electron-shells prevents their incorporation into these species. Therefore, when the evolving matter confronts with the Ca-rich rocks, mineralization of the aqua-complex components occur. As a result, argillaceous-limestone-organics sediments are replaced by a quartz-silicate-carbonate association with sulfide, hydrocarbon and graphite mineralization. Figure 2 illustrates such transformations. Kaolinite, the most abundant phase in the early minerals, corresponds stoichiometrically to the (Si, Al) aqua-complex (compare Fig. 1 and the scheme in Fig. 2). Its matrix acts as a nucleus for mineral transformations. Strain in the argillaceous-carbonate-organic matter caused by rock deformation (tectonics) and burial compaction need to be reduced. This could occur by extraction of elements with higher energies of bonding with O than Al has (120 kcal/mol), incorporating them into the aqua-complexes, and the formation through these intermediaries of new mineral phases. Carbonaceous matter however, universally distributed in sediments, prevents such metamorphic reactions. The only possibility of reducing the excess energy is to substitute Si by C in the left part of the aqua-complex. Such a replacement proceeds easily because C (2p²) and Si (3p²) have the same outer electron-shell structure, but the energy of C-bonds in oxygen tetrahedra (256 kcal/mol) greatly exceeds that for Si (190 kcal/mol). As sediments are subjected to deformation, the resultant energy balance in the mineral system is relaxed through the substitution of Si in clay by C. Organic matter provides reducing potential in the aluminosilicate matter, that is, in the network formed by kaolinite aqua-complexes. This stimulates their disintegration and reduction of the constituent radicals. The behavior of C is of particular interest. C⁰ generated during reduction can become graphite, and also it can participate in both oxidizing and reducing reactions to yield MCO₃ and C_nH_m products. At the point of redox transformation a metamorphic reaction proceeds (see Fig. 2). C_nH_m end products of this reaction cannot be regarded as completely new products. Primary humic and sapropelic organics are subjected to complex modifications and reworking on the clay matrix during diagenesis. First, together with carbonates, organics yield C to substitute for Si in kaolinite and other silicates. Second, an exchange of H and C occurs between the biogenic and mineral components of sediments. Third, at the expense of clay-carbonaceous material, vigorous synthesis of new hydrocarbon products occurs. Modified biogenic compounds are incorporated into the new phases, and this determines the complex characters of petroleum and other mature hydrocarbon products. Clay plays the role of a major reactive medium in these transformations due to the weak donor-acceptor and hydrogen bonds, which facilitate redistribution of chemical bonds within the aluminosilicate continuum.

4 Geologic and experimental evidence

The proposed processes seem to be taking place in the Solenoe Lake, located in the pre-Altai Kulunda steppe. Solenoe Lake is one of the numerous small lakes containing mineralized

water as several kilometers-wide chains (Fig. 2). The chains of lakes parallel the southwestern–northeastern extension of the main ridges of the Altai Mountains. In the Kulunda steppe, they are distinguished by coniferous forests. These features allowed us to suggest that mineralized lakes owe their

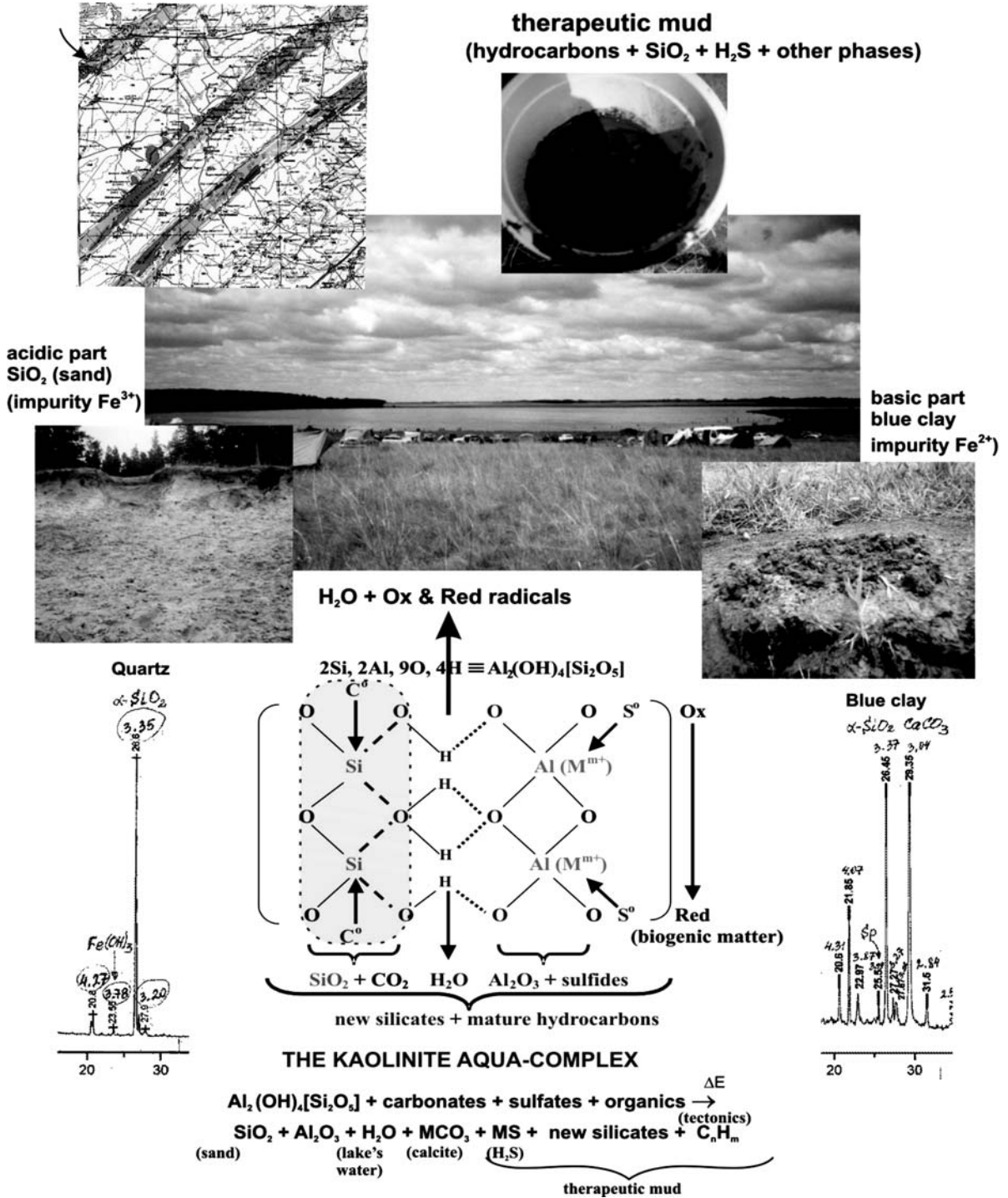


Figure 2: Geologic setting for the formation of hydrocarbons within a kaolinite matrix.

origin to the oscillatory fluctuations of tectonic strains caused by Altai orogeny. Rock deformations generate extra strain energies, which initiate our proposed reaction in sediments. The end products of this reaction are easily recognized in the Solenoe Lake (Fig. 2). Its left shore is composed of quartz sand.

Mineralized water of the lake itself stems from the water liberated from the central part of the aqua-complex. Hydrocarbon products are generated at the bottom sediments. Solid products of the reaction like new carbonates, silicates, and others are recorded by X-ray analysis of the clayey matter presenting the soil of the right lake's shore. It resembles true grey-blue clay. However, X-ray powder diffraction detected no peaks of the clay minerals (Fig. 2). On the other hand, careful examination illustrated dark masses that stand out in the light-colored clay. They differ from the light-colored "clay" in having a simpler composition, a lower content of CaCO_3 and a higher content of SiO_2 . TEM study showed that light-color argillaceous product is composed of well-faceted small crystals and larger amorphous particles. In the dark-colored "clay" no one well-faceted crystalline particle was observed. All products are presented by the fine poorly crystallized phases. The atomic structure of the semi-amorphous particles is apparent from HREM images that readily show the atomic rearrangements occurring within the clay matrix and explain why "blue clay" exhibits no peaks of clay minerals.

5 Conclusions

TEM and HREM data prove the mechanism of synthesis of hydrocarbon products on the clay matrix suggested on the basis of the aqua-complex concept. This mechanism combines previously antagonistic "organic" and "inorganic" viewpoints on the origin of oil and gas.

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