

### Bitumen–graphite transformation (after experimental data)

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The impact of temperature in hydrothermal media on model carbonaceous matter (CM) behavior was studied. The evolution of two types of CM in course of graphitization was described. The process results are favorable for metal concentration during deposits formation.

*Key words: carbonaceous matter, experiment, graphite, bitumen, gold*

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Purpose of the paper was investigation of metamorphism influence of on the carbonaceous matter (CM) composition and structure. Asphaltenes (As) and asphaltenic acids (AA) fractionated from the brown coals of the Pavlovskoye deposit (Primor'ye) have been chosen as the model matter. Chemical compositions of the initial As and AA are similar. The former differs only by the lower oxygen content (wt %): As: C – 75.13, O – 18.10, H – 6.54, AA: – C – 72.58, O – 19.98, H – 6.87. Hydrothermal experiments were conducted by the ampoule–autoclave method at 200, 300, 400, and 500°C,  $P_{H_2O} = 1$  kb. One of a number runs at room temperature and saturated water vapor pressure. Twice-distilled water, CM specimen (~50 mg) were put into the golden ampoule (10×100×0.2 mm) serving as a source of gold dissolution during run time. The last varied from 30 days at 200°C to 7 days at 500°C. Run products were fractionated onto the water fraction, soluble in alcohol–benzene mix at 50°C one and undissolved residue [Plyusnina et al., 2004].

The fraction soluble in alcohol–benzene (SF) is represented by a yellow oily liquid with a specific smell of oil. The gold concentration in it accounts for  $n \times 10^{-5}$  mol/kg at 200, 300°C, and  $n \times 10^{-4}$  at 400 and 500°C. Undissolved residue (UR), usually called kerogen, is represented by finely dispersed sootlike matter. The gold content in the kerogen is significantly higher than in the SF: for  $n \times 10^{-3}$  mol/kg at 200 and 300°C and  $n \times 10^{-2}$  mol/kg at 400 and 500°C.

IR-spectra of the kerogen synthesized at 400°C demonstrate that C–O bonds of carbonile and carboxyle acids (1340 and 1460  $\text{cm}^{-1}$ ) become less intensive, and the intensity of well-resolved aromatic group bands (750, 800, 850, and 1630  $\text{cm}^{-1}$ ) reaches its maximum. The absence of absorption bands of the groups C–H, CH= and CH<sub>2</sub> is an indication of the CM carbonization reactions. The absorption band near 1574  $\text{cm}^{-1}$  indicates on the graphitization of amorphous CM.

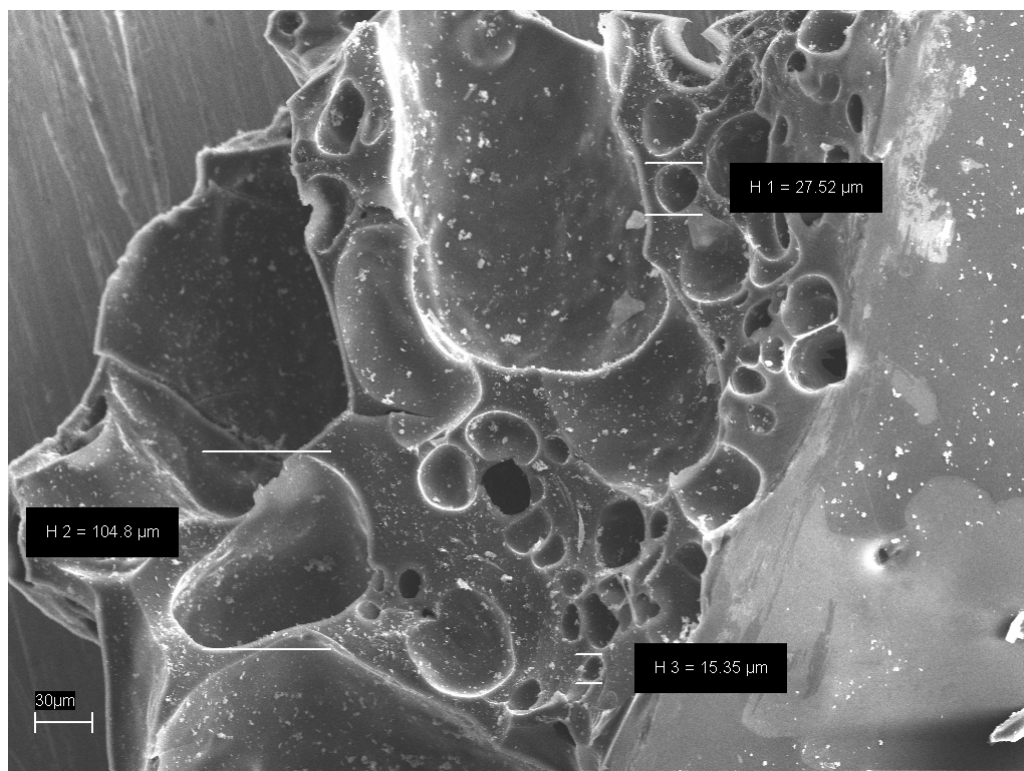
Kerogen formed at 500°C presents by black lustrous graphite-like flakes. Its X-ray photograph contains one peak of the main graphite lattice ( $d/n = 3.36\text{\AA}$ ). Thus, crystallization of weakly structured unordered graphite occurs at 500°C. Electron micrograph of graphite presents the globular microstructure (globules 200 to 500  $\mu\text{k}$ ). Our principal concern will be with the presence in the globules of rounded micropores with varying midship from 1 to 25  $\mu\text{k}$  (Fig. 1).

At the microscope numerous pores and channels in the cleavage interplane sites of graphite are observed to form a finemesh framework that may play the role of a molecular sieve analogous to those existing in zeolites. Apparently, it is a peculiar feature of graphite formed by thermolysis of bitumens. The presence of graphite micropore texture reflects devolatilization during the As thermolysis that is proved by great mass losses of the CM at experiments (Fig. 2). A rise in temperature is accompanied by a decrease of the primary mass by 10–90% in the 200–500°C interval.

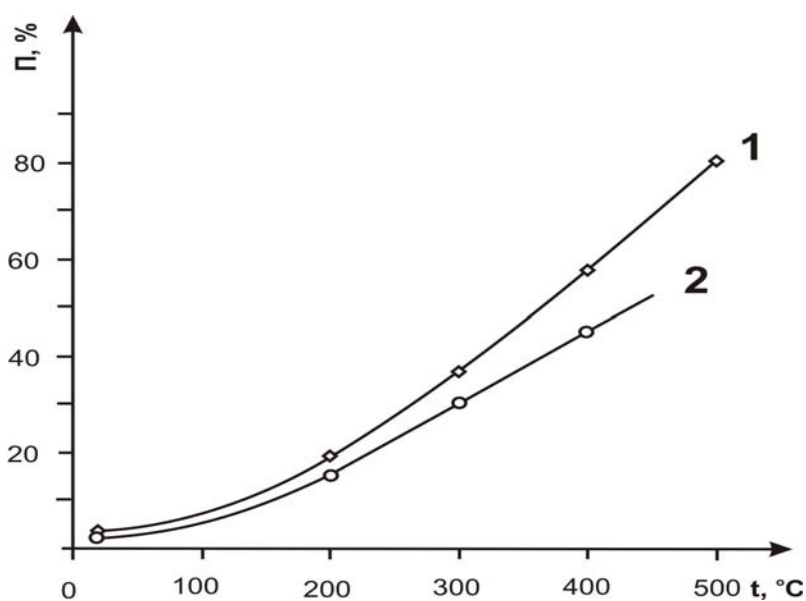
The relation of the UR and SF masses depends also on the temperature and experiments duration (Fig. 3). As a rule, the expense of the UR amount results in diminishing the SF mass. We have conventionally adopted the relation  $m_{UR}/m_{SF}$  as an aromatization coefficient ( $K_a$ ). According to the IR-spectra, the complete aromatization of the CM – aliphatic skeleton occurs at 500°C. Nevertheless, weak absorption bands of aromatic groups CO and COOH still remain. Such a

significant release of volatile components during the CM thermolysis ( $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{H}_2$  etc.) defines the redox-potential of the media [Plyusnina et al., 2009].

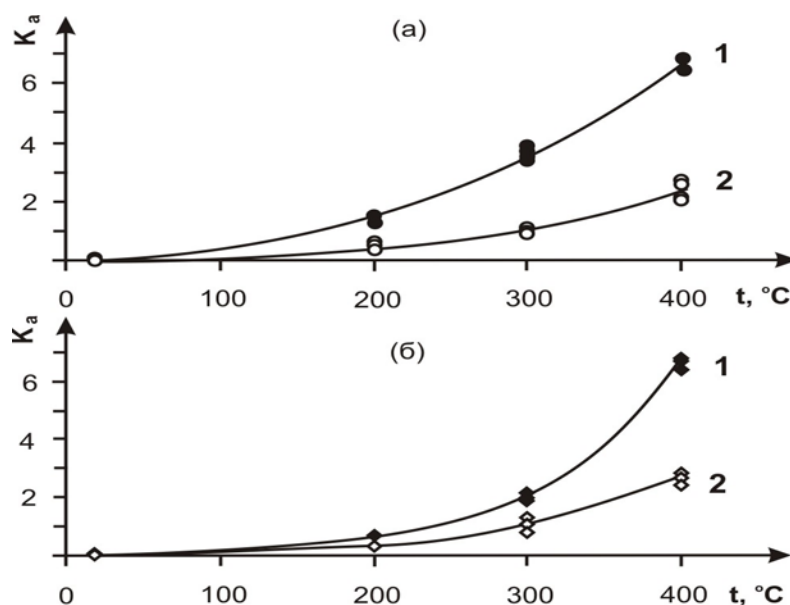
It ought to be noted that hydrothermal thermolysis of bitumens – graphite was obtained at  $500^\circ\text{C}$ . Earlier the complete graphitization during the CM dry pyrolyses occurred at  $1500^\circ\text{C}$  [Fischbach, 1971]. Our results on the start of the graphitization in the presence of aqueous fluid at  $P_{\text{tot}} = 1 \text{ kb}$  are closer to the nature and reflect the influence of pressure. It ought to be noted that graphitization is an irreversible process. Graphite is well preserved also at the superposition of retrograde metamorphism in nature.



**Fig. 1.** Globular micropore structure of the apoasphaltene (scanning electron microscope)



**Fig. 2.** Bitumens mass losses ( $\Pi$ ) as a function of temperature  
1 – As, 2 – AA;  $\Pi = (m_{\text{ini}} - m_{\text{fin}}/m_{\text{ini}}) \times 100$ ; m – mass: ini – initial, fin – final



**Fig. 3.** Coefficient of bitumen aromatization ( $K_a$ ) as a function of temperature (a) – As, (b) – AA; run time in hrs: 1 – more than 400; 2 – less than 240.  $K_a = mUR/mSF$

Thus, two mechanisms of metal concentration by the graphite are possible: chemisorption and filling of pores and channels of interlaminar space. The velocities of these processes are incomparable. The chemisorption occurs with relatively high rate: in 7 days at 500°C, the gold concentration becomes measurable in both CM fractions. Filling of pores and channels of kerogen has not been established in the runs. Possibly, it needs a longer term experiment, and may be the flow-type reactor model. In the natural conditions ore-bearing hydrothermal infiltration occurs during prolonged geological time. The discovered micropore texture of the apoasphaltene graphite is of a great interest. It reflects the influence of metamorphism on the volatilization reaction flow and formation of an unstable system at deconsolidation conditions favorable to the influx of hydrothermal ore-bearing solutions and metasomatic processes development.

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