TRACE ELEMENTS' FEATURES OF MATURE HYDROCARBON SYSTEMS

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According to the vertical evolutionary zoning of hydrocarbon formation (HC) with increasing depth, temperature gradient, pressure, and type of initial organics, the composition of HC systems in sedimentary sequence is transformed from immature (heavy) at shallow depths to degraded mature and ultramature (light) oils and condensates at large depths.

Highly transformed oils in the zones of catagenesis are characterized by the low contents of "biogenic" elements – V, Ni, and Fe. The total content of these elements is usually lower than 10 ppm. The oil is ascribed to either nickel (Ni > Fe > V) or iron (Fe > Ni > V) type. The degradation of the trace element (TE) composition of oils in the zone of catagenesis consists in the following. In the weakly degraded oils with relatively high content of primary asphaltic-resinous components inherited from initial OM, the total content of V, Ni, and other metals associated with heteroatomic compounds is higher than in the oil pools formed in more severe natural thermobarometric conditions, which cause partial loss of resinous-asphaltic matters. This is accompanied by the increase of light fractions and, correspondinly, increase of Cu, Fe, and occasionally, Pb contents in oils (Babaev and Punanova, 2014).

Let us exemplify the effect of catagenesis on the TE composition of oils in pools. The study of oils from Paleozoic sediments in the platform part of the Kama River region (Perm district) with relatively elevated content of resinous-asphaltic components showed the high vanadium and nickel contents in oils, i.e. TE is related to these components. The same sediments in the Cis-Ural foredeep host oils depleted in resinous-asphaltic components with trace elements dominated by Fe, Cu, and Pb. It is known that these elements are related to the lighter oil component. Paleotemperatures in the Paleozoic sediments of platforms and foredeeps sharply differ (by 50–120°C). Therefore, the observed differentiation in the trace element composition of oil is mainly caused by the influence of temperature (catagenetic) factor, which is stronger in the Cis-Ural foredeep than on the platform. Especially sharp differences between oil accumulations in platforms and foredeeps are observed in V/Fe and Ni/Cu ratios, which decrease systematically with growth of paleotemperatures in host sediments (Fig. 1).

Similar trace element trend was obtained for oils of the Paleozoic sediments of the southern Timan-Pechora PB, which are confined both to the subsided zones of the Izhma-Pechora basin and to the relatively uplifted zones of its western flank adjacent to the Timan region.
These data are supplemented by study of oils from Triassic sediments of the Prikumsk-Sukhokumsk zone of the Eastern Cis-Caucasus uplifts. These oils are light, sulfur-free, low-resin, highly paraffinic, with the low content of asphaltenes. The highly degraded oils are localized at great depths (from 3500 to 4500 m) in carbonates heated to 200°C according to vitrinite paleogeothermometry. Analytical studies showed that these oils are depleted in TE. The trends of TE indicators with a growth of oil catagenesis is preserved, i.e., oils show a decrease in the total V and Ni content (from 6.8 to 0.5 ppm), and decrease in V/Fe ratio from 3.4 to 0.15 and (V + Ni)/(Fe + Cu) ratio from 2.2 to 0.08 (Punanova and Chakhmakhchev, 1992).

The variation trends of TE and their ratios in oils depending on paleotemperatures and burial depths of host rocks are mainly preserved for OM bitumoids. Definite difficulties in revealing the dynamics of degradation of TE composition of dispersed OM in rocks highlight the need

to consider these catagenetic changes in the OM of definite facies – genetic type. The study of the effect of catagenesis on the traceelement composition of syngenetic chloroform bitumens (CBA) of the domanik sediments of the Timan-Pechora PB localized at depths from 0 to 6000 m under different paleotemperature conditions (from 100 to 230°C, transformation stages MC_1–MC_3) showed that an increase of catagenesis is accompanied by the decrease of the total vanadium and nickel content from 2400 to 160 ppm, V/Fe ratio from 21.0 to 0.6, and V/Pb ratio from 130.0 to 4.7 (Chakhmakhchev et al., 1983). The same trend was established in CBA of deeply buried Triassic sediments of the Prikumsk-Sukhokumsk uplift zone of the Eastern Cis-Caucasus (3500–5200 m), with the directed decrease of V content (from 2200 to 500 ppm) and trace element ratios V/Fe (from 10 to 0.1), Ni/Cu (from 20 to 0.1), and Co/Zn (from 2 to 0.02) with depth.

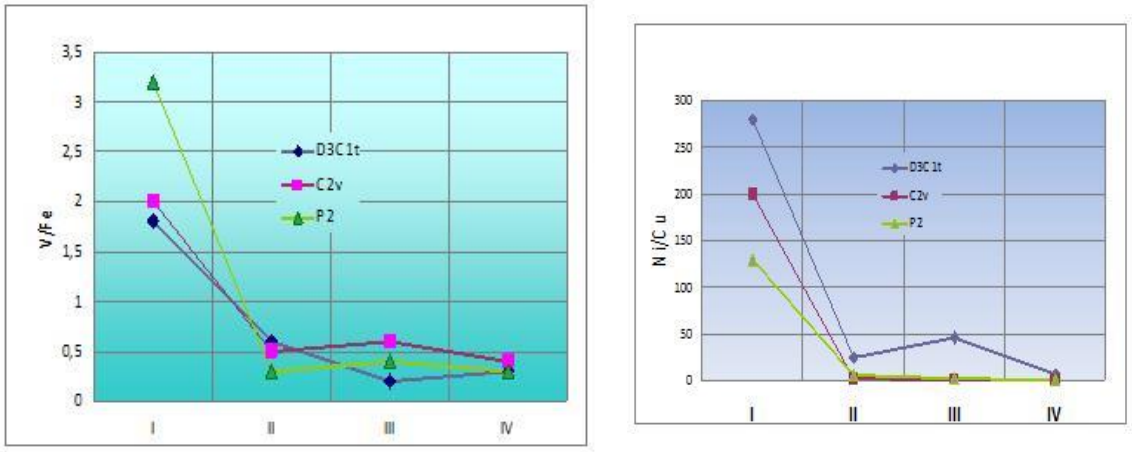

Figure 1. *Trace element indicators of maturity of oil from Devonian, Carboniferous, and Permian sediments of the Cis-Urals (Perm district) in relation with their different structural position and paleotemperatures. I – Bashkirian and Permian arcs, tpaleo = 100–145°C; II – Solikamsk Basin, tpaleo = 145–170°C; III – Kos'va-Chusov saddle, tpaleo = 170–190°C; IV – Yuryuzan-Sylven basin, tpaleo = 190–250°C.*

Thus, the study of the dynamics of TE variations in oils and OM of rocks by the example of the Volga-Ural, Timan-Pechora, Cis-Caucasus, and other PB showed that the increase in the thermocatalytic degradation of oils is accompanied by significant decrease of elements related to the heteroatomic components and decrease of V/Fe, V/Cu, V/Pb, Ni/Cu, and other ratios. The diagnostic indicators of the thermal maturity of OM and oils most clearly manifest themselves for sapropel initial OM in the mature oil generation zone in the interval of Ro from 0.6 to 1.1%, more rarely 1.3%. These ratios well correlate with such geochemical index of catagenetic degradation of oil HC as cyclohexane to cyclopentane ratio in benzine fraction (Punanova and Vinogradova, 2016).

References

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