EFFECT OF CO_2 ON $\delta^{13}C$ AND δD ISOTOPE TYPE-CURVES OF OILS AND CONDENSATES DURING MIGRATION (NW PANNONIAN BASIN, HUNGARY)

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Evaporative fractionation is well-known in many regions of the world (e.g. the Gulf Coast, the Alaskan North Slope, the North sea, the south China Sea, Taiwan, Indonesia, the Eastern Carpathians in Poland, etc; Meulbroek, 2002), which is the physico-chemical alteration of petroleum components, the solution and exsolution in saturated hydrocarbon gases generated in or arrived to a reservoir. The driving force is the continued charge of mature hydrocarbon gas. Carbon dioxide may have similar effect as mature hydrocarbon gases. Kvenvolden and Claypool (1980) demonstrated CO_2 transported gas and gasoline-range hydrocarbons in solution in Alaska. McKirdy and Chivas (1992) also presented that supercritical CO_2 extracted and transported gasoline-range hydrocarbons in Australia. Earlier in the USSR (at Inst. Geol. and Exploit. Min. Fuels) there was intensive research; results of Sokolova and Mironov (1962) have proved that both CO_2 and CH_4 can dissolve considerable amount of oil. They studied the transformation of organic matter under the action of compressed gases, and stated that the qualitative composition of hydrocarbons would differ from the composition of the hydrocarbons and other petroleum components liberated from rock during the primary migration.

Later, the role of CO_2 in enhanced oil recovery (EOR) became important, and the effect of its injection was studied (e.g. Hwang and Ortiz, 2000). Recently, Lifshitz et al. (2012) demonstrated that supercritical CO_2 extraction is a highly selective method, extracting predominantly hydrocarbons from carbonaceous materials regardless of their facial type, and the extract is enriched in alkanes and cycloalkanes,

During this decade has increased the interest for the Répcelak-Mihályi Field (north western part of Hungary). This field has CO_2, hydrocarbon, and mixed gas pools. The CO_2 fields are located about 1400 m depth in the Pannonian sedimentary sequences (mainly late Miocene sandstone, siltstone and clay). In earlier study the oil traces were analyzed, but it was only a side-issue. The isoprenoid and light to heavy n-alkane were determined by gas chromatography of some sample oil and condensate traces. Two groups were distinguished, one of them was deposited in anoxic, the other in oxic conditions (Vető et al., 2014).

In the present study we applied more analytical methods, including the D/H and $^{13}C/^{12}C$ ratios, to get a more complete view of the origin of oils and condensates. Another oil sample was studied from 20 km to east from M22 oil to get idea about the source rock.

The $^{13}C/^{12}C$ type-curves show very unusual shapes. Compared to earlier oil and condensates measurements M13 and Mf3 type-curves are unique. In these samples the $^{13}C/^{12}C$ ratio of aromatic hydrocarbons (HCs) is lower than that of saturated HC. Their aromatic HC contents on the basis SARA measurements are extremely low (0.28 and 0.82) comparing to those of the others (2.45-27.4).

The exsolution of aromatic HC and resin (NSO) in CO_2 solute was found earlier by Sokolova and Mironov (1962), Lifshitz et al. (2012) and Galimov et al. (1985) in experimental series. Galimov et al. (1985) also have found the isotope ratio to decrease.

The D/H type-curves are similar to the earlier measured ones. M22 (pr/ph=0.8) oil is the most negative and Vasz-1 (pr/ph=1.54) is the least negative. This great difference is reflected in their pristane/phytane ratios and $C_{35}\alpha\beta(S)/C_{34}\alpha\beta(S)$-hopane ratios too.

It was supposed that the considerable difference between oil and condensate samples is caused by supercritical CO_2 arriving into a reservoir and some part of oils or condensates migrated dissolved in CO_2 and were accumulated in a reservoir and changed composition like in the case evaporative fractionation driven by mature hydrocarbon gas. The results corroborate our idea.
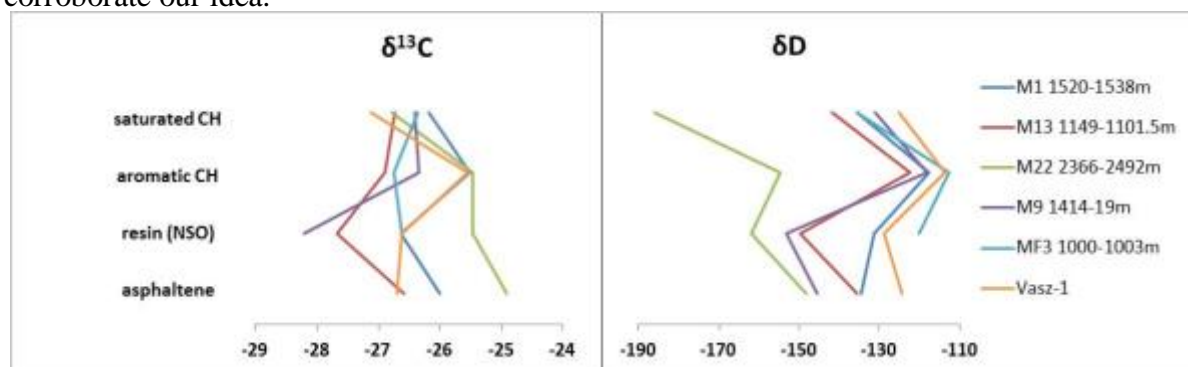

Figure 1. *Isotope type-curves of the oils and condensates.*

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