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Vanadium, Ni, S and Hg contents in Bulgarian crude oils: Genetic and environmental implications

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Съдържание на V, Ni, S и Hg в български нефти: генетични интерпретации и екологични съображения

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Abstract. We report new V, Ni, S, and Hg data for four condensates and seven crude oils from Central Northern and Eastern Bulgaria. The samples have relatively low trace metal contents compared with other published crude oils and condensates. These properties facilitate their production and reduce environmental concerns for trace metal release from the processed products. Low S contents at moderate Ni/V ratios for all oils from Central Northern Bulgaria suggest origin from clastic source rocks deposited in mildly reducing conditions. In contrast, the Tyulenovo oil from Eastern Bulgaria has high Ni/V ratios at low S contents, indicating possible origin from lacustrine source rocks.

Keywords: trace metals, mercury, condensate, petroleum, Bulgaria.

Introduction

Given appropriate time, temperature and organic matter (OM) type and amount, the thermal maturation of sedimentary rocks can ultimately lead to the generation of hydrocarbons (bitumen, oil and gas). Crude oils often preserve direct genetic links to their source rocks in the form of biologically-derived organic molecules (biomarkers). In addition, crude oils inherit some of the trace metals from the sedimentary OM and thus trace metal contents and ratios can provide information on the origin of the oils, including their source. On the other hand, even minute amounts of trace metals like V, Ni and Hg as well as common oil constituents like S, pose technological challenges during oil processing, acting like catalytic poisons, and being particularly damaging through corrosion (e.g., Speight, 2016; Wilhelm, Bloom, 2000). The release of these elements into the environment through petroleum processing and fuel oil burning leads to atmospheric, aquatic and soil pollution. In higher concentrations, these elements can pose hazards to ecosystems and human health. For example, Hg, SO_2 and HS are known for their toxicity. Here, we present the first trace metal data for Bulgarian crude oils and condensates and

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discuss their genetic applications and technological and environmental significance.

Geological background and samples

Bulgarian petroleum reserves are concentrated in the Moesian Platform, which formed in the Mesozoic on the southern Eurasian margin (Dabovski, Zagorchev, 2009). A large volume of geophysical, mainly gravimetric and magnetometric studies carried out between 1947–1950 (see overview in Marinovska, Botoucharov, 2021) led to the discoveries of industrial reserves of heavy oil in carbonates of the Lower Cretaceous Kaspichan Formation in the Tyulenovo oil field in 1951. Systematic geological, geophysical and drilling exploration activities for oil and gas then focused on the so-called "Pleven gravitational maximum" in Central Northern Bulgaria (e.g., Georgiev, Atanasov, 1993). During 1962–1989, a series of oil, gas-oil and gas condensate deposits were discovered within the Middle Triassic limestones and dolomites of the Doirentsi Formation (Dolni Dabnik, Gorni Dabnik, Devetaki, Pisarovo, Aglen and Selanovtsi fields) and the Lower Jurassic sandstones of the Kostina Formation (Dolni Lukovit, Bardarski Geran, Marinov Geran and Butan fields). The latest onshore hydrocarbon deposit, Iskar-west gas condensate field, was discovered in 2013 within the Kostina Formation. Samples for this study include light oils and condensates from the Dolni Dabnik, Dolni Lukovit and Staroseltsi and Selanovtsi fields with methane, high paraffin and low resin composition, as well as Lower Jurassic oil and condensates from Burdarski Geran, Marinov Geran, Iskar-west and Butan and a heavy oil from Tyulenovo.

Table 1. S, V, Ni and Hg contents in studied samples

Sample type	Location	S	V	Ni	Hg
		ppm (μg/g)	ppm (μg/g)	ppm (μg/g)	ppb (ng/g)
Condensate	Dolni Dabnik	365	0.11	2.69	N/A
Condensate	Iskar-west	830	<0.001	<0.06	98.2
Condensate	Marinov Geran	241	0.12	0.56	3.53
Condensate	Butan	260	0.014	0.52	5.97
Crude oil	Dolni Dubnik	1214	0.13	0.26	5.86
Crude oil	Dolni Lukovit	782	0.93	1.62	6.97
Crude oil	Dolni Lukovit-west	1370	0.93	0.94	3.74
Crude oil	Staroseltsi	1065	1.17	1.25	5.31
Crude oil	Selanovtsi	4061	10.97	7.40	5.41
Crude oil	Selanovtsi	N/A	8.40	6.99	N/A
Crude oil	Burdarski Geran	1235	0.34	0.60	6.56
Crude oil	Tyulenovo	3433	0.24	3.85	4.95
Crude oil	Tyulenovo	N/A	0.25	3.75	3.15

N/A – not analyzed. The number of decimal places is related to the precision of the measurements.

Methods

Seven crude oils and four condensates (~0.2 g each) were decomposed at the Faculty of Chemistry and Pharmacy, Sofia University (FCP–SU) and at the Geological institute, Bulgarian Academy of Sciences (GI–BAS) either by microwave acid digestion or hotplate acid digestion in closed PFA vessels using a mixture of conc. HNO_3-H_2O_2. Trace metal contents were measured on Perkin Elmer SCIEX DRC-e ICP-MS at FCP–SU and at GI–BAS. Matrix-matched standards NIST SRM 1634c (residual fuel oil) and NIST RM 8505 (crude oil) yielded the following recoveries: Ni (81–107%), V (76–113%) and S (104%). Hg contents of the samples were measured on a DMA instrument at GI-BAS (see Georgiev, Bidzhova, 2023 for additional details).

Results

The S contents of the studied samples vary between 241 ppm and ~0.4 wt% (Table 1), with most of the crude oils containing higher amounts of S (~1000 to ~4000 ppm) compared with the condensates (241–830 ppm). Similarly, V (0.13–11.0 ppm) and Ni (0.3–7.4 ppm) contents in the crude oils are higher than in the condensates (0.01–0.12 ppm V and 0.5–2.7 ppm Ni, respectively. Whereas Hg contents in most crude oils and condensates vary in narrow limits (3–7 ppb), the Iskar condensate is significantly enriched in Hg (98 ppb).

Discussion

Vanadium, Ni and S abundances in crude oils and related products vary widely (e.g., Lewan, 1984; Barwise, 1990). Compared with most published data, the studied Bulgarian oils have lower S, Ni and V concentrations (Fig. 1a). Mercury contents in worldwide crude oils and condensates also vary over several orders of magnitude (e.g., Wilhelm, Bloom, 2000). The narrow (3–7 ppb) range of all Bulgarian crude oils and most condensates is generally towards the lower end of published data. Although clearly higher than the remaining samples, elevated mercury levels in the Iskar condensate (98 ppb) are not unusual for condensates in general, which tend to be more enriched in Hg compared with crude oils and can reach concentrations of several thousand ppm Hg (Wilhelm, Bloom, 2000). Overall, the relatively low abundances of S and trace metals, Hg in particular, in the studied Bulgarian oils suggest low risk of potential fuel production complications and of environmental and health hazard issues.

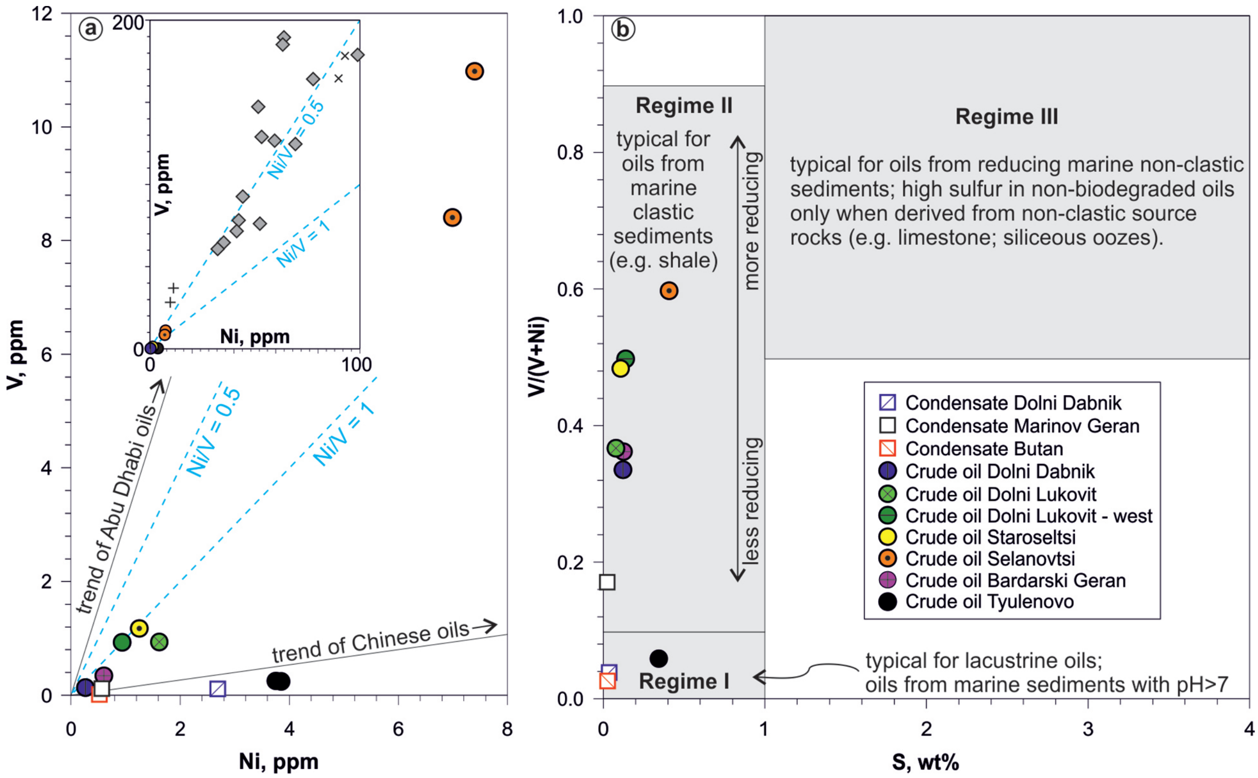

Fig. 1. V-Ni-S contents and ratios in studied oils and condensates. Panel (*a*) shows the V and Ni contents and trends typical for crude oils from carbonates sources (Abu Dhabi oils) and from lacustrine sources (Chinese oils), based on the work of Barwise (1990). Blue lines show constant Ni/V ratios. The inset shows V and Ni contents of the studied samples compared with V and Ni contents of Lower-Middle Jurassic potential source rocks from Northern Bulgaria (gray diamonds; data from Georgiev et al., 2022) and to unrelated oils from carbonate sources (x symbols; Noto oil, Sicily; Georgiev et al., 2016) and from shale sources (crosses; Brynhild oil, North Sea; Georgiev et al., 2019). Panel (*b*) shows the relationship between V proportionality (V/V+Ni) and sulfur contents, with the characteristics of the three major regimes outlined by Lewan (1984). See text for additional details.

Vanadium and Ni are the two most abundant trace metals in petroleum, typically in the tens to thousands ppm levels. They are also most widely used for genetic interpretations, following primarily the work of Lewan (1984) and Barwise (1990) summarized below. In brief, V and Ni are transferred from the water column into sedimentary organic matter in a proportion depending on the redox potential, pH and sulfide ion availability. The two metals are hosted primarily in porphyrin complexes (derived from chlorophyll precursors) and high-molecular weight organics. Even though the thermal maturation of OM, expulsion of oils and secondary processes may change the V and Ni contents of the various components, the proportion of the two metals is expected to remain relatively unchanged and close to the original proportion in the source rock. Sulfur contents in particular are readily affected by secondary processes such as biodegradation, which usually raises S concertation in biodegraded oils.

The interplay between these geologic factors and their effects on oil composition offers insights into the origin of petroleum. For example, reducing conditions during sediment deposition favor V precipitation into OM, whereas basic conditions act in the opposite manner. Sulfate availability plays an important control on organic Ni. In lacustrine settings lacking sulfate ions, Ni is readily available to bond with OM, whereas in sediments with significant activity of sulfate reducing bacteria most Ni is bound as sulfides, thereby decreasing Ni availability for binding with OM. Sulfur contents in crude oils derived from carbonate sources are generally higher, as these sediments lack reactive Fe to bind sulfide ions into pyrite, whereas shale-derived oils usually have lower S contents due to their abundant reactive Fe binding S into pyrite. As a result, three major groups of crude oils are distinguished based on their V-S-Ni contents (Fig. 1b; Lewan, 1984): high Ni-low V-low S regime for oils derived from lacustrine rocks (regime I); high V-low Ni-high S regime for oils derived from carbonate sources (regime III), and an intermediate regime of low S oils with variable V and Ni, derived from variably reduced clastic marine sediments (regime II). Similarly, high Ni/V ratios are characteristic for oils derived from lacustrine source rocks (Fig. 1a; Barwise, 1990).

Most Bulgarian oils in this study are characterized by low V, Ni and S contents and V proportionality (V/V+Ni) between 0.33 and 0.60 and fall into the second regime of Lewan (1984). Their characteristics suggest these oils originated from clastic marine sediments deposited in mildly reducing to mildly oxidizing conditions. Regional studies supported by biomarker oil-source correlations identify shallow marine Lower to Middle Jurassic sediments from Northern Bulgaria as the likely source rock for these oils, and particularly the organic-rich shales of the Etropole Formation (Stefanets Member) (Georgiev, 2000). Based on trace metal data, these clastic sediments were deposited in an overall oxygenated environment with periodic dysoxia to anoxia (Georgiev et al., 2022), i.e. mostly within Regime II on Fig. 1b. The Ni/V ratios for all oils except Tyulenovo vary between 0.7 and 2 partly overlap with published Ni/V ratios for Jurassic shales (Fig. 1a-inset), supporting a possible origin from Jurassic source rocks.

Notably, the Tyulenovo oil from East Bulgaria has consistently lower V proportionality of 0.06 compared with all other Bulgarian oils. Together with the low S contents, this is a feature characteristic of Regime I (Fig. 1b), indicating possible origin (or contribution) from lacustrine source rocks. On a V-Ni diagram (Fig. 1a), the high Ni/V ratios (15–16) of the Tyulenovo samples deviate from the remaining oils and resemble the trend of Chinese oils derived from lacustrine rocks. A different origin for the Tyulenovo oils compared with the remaining Bulgarian oils was also suggested based on their different organic biomarker profiles (Georgiev, 2007; Mayer et al., 2018). Condensates from Central Northern Bulgaria also show lower (V/V+Ni) and higher Ni/V ratios than crude oils from this region. Similarly to Tyulenovo oil, these features may point to lacustrine source rocks contributions. However, they may be related to the gas phase origin and the compositional difference between condensates and crude oils from Central Northern Bulgaria. Expanding the trace metal dataset with other crude oils, condensates and source rocks from Northern Bulgaria can reveal additional genetic links between them.

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