Sulphur Compound Distributions in the Upper Jurassic Source Rocks from the Dinarides

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The distribution of elemental sulphur and sulphur bound in inorganic and organic compounds was investigated for three surface samples of the oil-source rock from the Upper Jurassic strata in the Dinarides.

Concentrations of elemental sulphur are very low and the concentrations of sulphur bound in pyrite and sulphates are relatively low. On the other hand, organically-bound sulphur in both kerogens and bitumens is rather high, representing almost a tenth of the bitumens and the kerogens by weight.

Among the organo-sulphur compounds in bitumens, analyzed by GC-MS, alkylthiophenes, alkylbithiophenes, alkylthiolanes, alkylbenzothiophenes and alkyldibenzothiophenes were identified. Among the pyrolysis products of kerogens alkylthiophenes, alkenylthiophenes and benzothiophenes were identified.

Based on similar sulphur distribution and the same organo-sulphur compounds identified in the bitumens and kerogen pyrolysates, samples are thought to be geochemically related.

The extremely high concentrations of organic matter and of organically-bound sulphur indicate that the depositional environment of the Upper Jurassic strata in the Dinarides was most probably anoxic and iron lean.

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INTRODUCTION

Contemporary theories on oil (petroleum) formation are based on the concept of oil generating basins.[1] This implies the existence of an oilsource rock (OSR),[2] which consists of a mineral matrix and of organic matter (OM) of bio-mass origin, as precursor of oil. OM in OSR is composed of kerogen (non-soluble geo-macromolecules) and bitumen (soluble, low-molecular weight organic matter). Oil generation is explained[3] by thermo-catalytic cracking (catagenesis) of kerogen, as oil precursor, into relatively small organic molecules, mainly hydrocarbons, which, by migration in geological traps (oil basins), accumulate as oil.

On the surface of the Dinarides, three OSR of Mesozoic age have been determined: Triassic, Upper Jurassic and Cretaceous.[4,5] They contain a predominantly carbonate mineral matrix and are relatively rich in OM, especially the Upper Jurassic OSR. The organic-rich geological strata (total organic carbon > 0.5%) with predominating carbonate mineral matrix were supposed to contain remarkable amounts of sulphur compounds. This was confirmed by Tissot and Welte,[3] who determined 0.9% as the average value for sulphur in 2464 samples of this OSR type.

Sulphur in OSR might be present as elemental sulphur or in inorganic and organic compounds. Inorganic compounds, pyrite and sulphates are interesing since they can reflect the environmental conditions during deposition of the OSR.[6] Pyrite reflects geological events when anoxic conditions (low Eh) prevailed. Such conditions favour preservation of sedimented OM and improve the chances of a good oil-prone OSR generation. In contrast, sulphates reflect oxic conditions prevailing during deposition (Eh was high), thereby diminishing the probability of OSR formation. Sulphates might also postdepositional proceed from pyrite by oxidation after uplifting and exposure to the atmosphere.

Organic sulphur might be distributed in kerogen and in bitumen. Incorporation of sulphur into kerogen is thought[7,8] to happen during early diagenesis of the deposited OM if metal ions, especially iron, are not present. J. S. Damste and coworkers[9] explained that, upon maturation, sulphur-rich kerogen releases, among others, low-molecular-weight (Lmw) organo-sulphur compounds which to some extent mirror the sulphur-containing structural units present in the kerogen.

Lmw organic sulphur compounds might be released from kerogen also artificially by pyrolysis. The released structural units containing sulphur may also represent the structure of the pyrolyzed kerogen.[10]

The occurrence of organo-sulphur compounds in kerogen and/or bitumen indicates[11] the low Eh deposition environment favouring preservation of OM, potentially resulting in good-quality source rocks.

To study the occurrence of sulphur compounds in the Upper Jurassic OSR, the most organic-rich in the Dinarides, elemental sulphur, pyrite and sulphatic sulphur, as well as organically-bound sulphur, were investigated. The results are expected to reveal the conditions in depositional environment for that OSR, and to improve our knowledge of the genetic relations of the OM studied.

EXPERIMENTAL

Three geochemical samples, marked D1, D2 and D3, from the Upper Jurassic strata were taken from the surface of the Dinarides (Figure 1). Samples were chosen from deeper surface layers in order to minimize atmospheric influence.

Each sample, ground to the size of 100 µm in a rotary disc mill, was subjected to analyses of elemental and inorganically-bound sulphurs, and to Soxhlet extraction by $CHCl_3$.

Elemental sulphur was examined by activated copper.[12] Ground samples were mixed with copper particles and observed for occurrence of stains. In pyrite, sulphur was calculated through a stoichiometric combination with iron, and sulphur in sul-
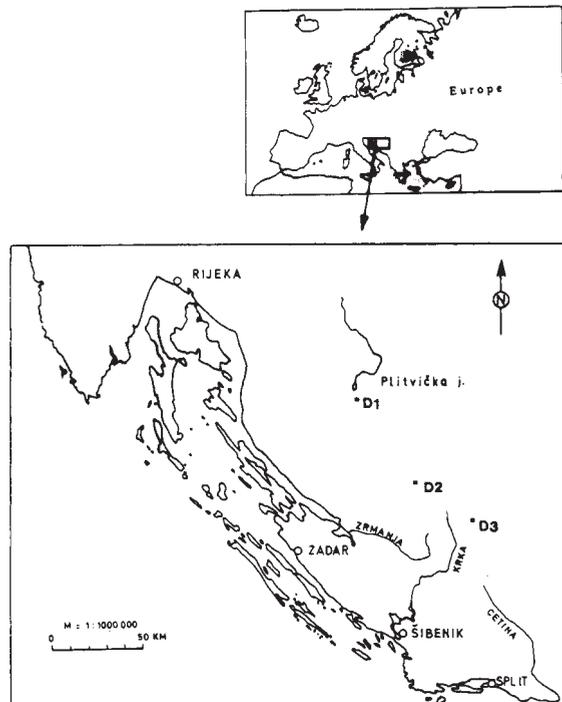

Figure 1. Sample location.

phates was determined by the gravimetric method.[13] Sulfate sulphur was extracted from the ground sample with diluted hydrochloric acid. Sulphates are soluble in hydrocloric acid, but pyrite and organic sulphur are not. After determination of sulphate sulphur, pyrite was destroyed by diluted HNO_3 and the concentration of Fe^{2+} was determined.

Bitumen was fractionated by column chromatography, using *n*-hexane and toluene as solvents. The column (50 cm × 10 mm) was packed with an equal volume of alumina (top) and silica (bottom). Both were activated for 1 h at 150 °C.

The toluene eluate, shown to contain sulphur by elemental analysis, underwent further fractionation in order to obtain less complex mixtures. Subfractionation was performed by column chromatography on activated alumina into three sulphur-containing (SC) subfractions with mixtures of *n*-hexane and toluene:

SC1 subfraction by *n*-hexane + toluene = 3 + 1,
SC2 subfraction by *n*-hexane + toluene = 1 + 1,
SC3 subfraction by *n*-hexane + toluene = 1 + 3.

The SC subfractions were submitted to the GC-MS analysis.

After extraction, the ground residues were subjected to pyrolysis in a flow (N_2) tube reactor[14,15] at 550 °C for 15 min. Pyrolysis products were collected into cooled *n*-hexane or decahydronaphthalene.

For identification of organo-sulphur compounds in SC subfractions and pyrolysates, GC-MS was used under the following conditions:
GC: fused-silica column, non-polar, SPB-1, 60 m; temperature programme: 50 °C, 10 °C/min to 220 °C, final temperature for 30 min; carrier gas: He; MS: ion source: electron impact; electron energy: 70 eV; emission current: 0.7 mA; resolution: 1 to 500; ion source temperature: 200 °C, ion source pressure: 10^{-5} Pa.

For identification, full mass spectra and mass fragmentograms were used.

The thiophenic ratio of the pyrolysate as defined by T. Eglinton *et al.*[10] [2,3-dimethylthiophene/(*n*-nonene + 1,2-dimethylbenzene)] was determined by means of GC. The related components were identified by the GC-MS and confirmed by GC analysis using reference compounds. Quantification was performed by flame ionization detection with no correction factors.

GC conditions were as follows:
column: fused silica, non polar BP-1, 25 m; temperature programme: 40 °C for 15 min, 15 °C/min to 280 °C, final temperature for 30 min; carrier gas: H_2; injection mode: splitless 30 s.

Elemental analysis of (organically-bound) sulphur and carbon in bitumen and in kerogen, isolated by the procedure described by Durand,[2] was performed. Sulphur in bitumen and kerogen was determined by te method described in the DIN standard.[16] Sulphur was converted by combustion and oxidation to sulphur(VI)-oxide, which in reaction with water gave sulphuric acid, and the sulphate ion was determined gravimetrically. Carbon in bitumen and kerogen was determined by the procedure after Pregl.[17] Organic matter was burnt in the presence of oxygen and the amount of carbon was determined by the stoichiometric ratio of C and CO_2.

Organic carbon in the bitumen and organic carbon in the kerogen obtained by elemental analysis are expressed in the paper as the percentage of total organic carbon (TOC).

RESULTS AND DISCUSSION

Sulphur distribution in the Upper Jurassic OSR samples D1, D2 and D3, taken from the surface of the Dinarides, was studied.

According to the results achieved, the contribution of elemental sulphur can be neglected since no stains were noticed on copper particles after mixing them with any of the (ground) samples.

Pyritic and sulphate sulphur are rather low in D1 and D2 (Table I) though present in each of the samples. In sample D3, the richest in OM and in total sulphur, the inorganic sulphur represents 1.43% of the whole sample by weight.

The presence of pyrite and high TOC values (Table I) point to favourable anoxic conditions during sedimentation. The pesence of sulphates indicates plausibly that the samples underwent partial oxidation of pyrite after the uplifting and exposure to the atmosphere.

In the OM, sulphur was found to reach a tenth of the kerogen by weight plus a similar percentage in bitumen in each sample. For the most oil-prone D3 (TOC = 53.8%), organically-bound sulphur contributes up to 7.8% (wt) of the whole rock sample (Table II).

TABLE I

Contents of sulphur from sulphates and pyrite in relation to TOC
(total organic carbon)

Sample	w(S) from sulphates,%	w(S) from pyrite,%	w(C) from kerogen,%	w(C) from bitumen,%	TOC,%
D1	0.05	0.02	17.1	2.7	19.8
D2	0.04	0.01	5.7	1.0	6.7
D3	1.24	0.19	50.0	3.8	53.8

TABLE II

Sulphur in organic matter of the Upper Jurassic source rock

Sample	Organic matter		Σ Organic matter (kerogen+ bitumen), %	w(S) in kerogen,%	w(S) in bitumen,%	Σw(S) from organic matter,%
	Kerogen, %	Bitumen, %				
D1	23.20	3.60	26.80	10.12	8.89	2.67
D2	7.91	1.35	9.26	11.89	9.52	1.07
D3	76.58	5.10	81.68	9.52	9.74	7.80

GC-MS analyses of sulphur-containing organic compounds in the bitumen showed that they are present as minor components in rather complex mixtures. The SC subfractions were found to be composed of a large number of *n*-, *iso*- and cycloalkanes, as well as alkylbenzenes, alkylnaphthalenes and alkylphenantrenes and/or alkylanthracenes. Many isomers of these aromatic hydrocarbons were recorded and the range of intensities was large, causing a vast overlap of mass spectra. This limited the number of the positively identified sulphur-containing constituents. Skeletons were determined for the identified compounds, but no detailed structure, including the position(s) of alkyl-group(s), could be established.

Each of the identified sulphur-containing compounds, found in one of the SC subfractions, seems to be present (according to mass spectra and to GC retention data) also in the two related ones (for example: the component identified in SC1 subfraction of D1 seems to be the same as in SC1 subfraction of D2 and of D3). In identification of molecular ions, the specific (diagnostic) ions and their intensity ratios were used. Specific ions were studied in full mass spectra and they were additionaly scanned as mass fragmentograms. For instance, the range of masses m/z 111, 125 and 139 were recorded for the alkylthiophenes and masses m/z 109, 123 and 137 for alkenylthiophenes. Non-aromatic hydrocarbons with the same molecular weight were discriminated from sulphur containing compounds by the absence of the characteristic decreasing range of low mass fragments and by the low intensity of molecular ions. Aromatic hydrocarbons were recognized according to molecular ions, their intensity and specific ions (reference compounds were applied for the range of *n*-alkylbenzenes: *n*-octylbenzene up to *n*-tetradecylbenzene).

In the SC1 subfractions (Table III), alkylbenzothiophenes, such as heptylbenzothiophene, nonylbenzothiophene and undecylbenzothiophene, alkylbithiophenes such as four isomers of nonylbithiophenes, and alkylthiophenes such as dodecyl-, tridecyl- and tetradecylthiophen, were determined.

In SC2 subfractions, six isomers of nonylbithiophenes and five isomers of octadecylbenzothiophenes were identified. Also, among alkylthiolanes two isomers of dodecylthiolane, one tridecylthiolane and three isomers of octadecylthiolane were determined (Table IV).

In SC3 subfractions, organo-sulphur compounds such as alkyldibenzothiophenes, thiophenes and alkylbithiophenes (Table V) were identified: three isomers of ethyldibenzothiophene and four isomers of decylthiophenes, three isomers of octylbithiophene, four isomers of nonylbithiophene and three isomers of decylbithiophene.

Identified thiolanes are present in SC2 subfractions, and dibenzothiophenes in SC3 subfractions.

The specific ion m/z 221 pointed to the presence of bithiophene and the molecular ion M$^+$ 292 confirmed nonylbithiophene (Figure 2). Mass differ-
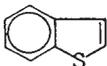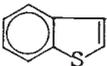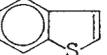
TABLE III

Sulphur compounds identified in SC1 subfraction

Sulphur compound		Molecular mass
7C—	heptylbenzo(b)thiophene	232
9C—	nonylbenzo(b)thiophene	260
9C—	nonylbithiophene (4 isomers)	292
12C—	dodecylthiophene	252
11C—	undecylbenzo(b)thiophene	288
13C—	tridecylthiophene	266
14C—	tetradecylthiophene	280

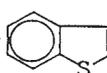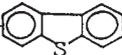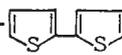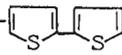TABLE IV

Sulphur compounds identified in SC2 subfraction

Sulphur compound		Molecular mass
12C—	dodecylthiolane (2 isomers)	256
9C—	nonylbithiophene (6 isomers)	292
13C—	tridecylthiolane	270
18C—	octadecylthiolane (3 isomers)	340
18C—	octadecylbenzothiophene (5 isomers)	386

TABLE V

Sulphur compounds identified in SC3 subfraction

	Sulphur compound	Molecular mass
2C— (ethyldibenzothiophene structure)	ethyldibenzothiophene (3 isomers)	212
10C— (decylthiophene structure)	decylthiophene (4 isomers)	224
8C— (octylbithiophene structure)	octylbithiophene (3 isomers)	278
9C— (nonylbithiophene structure)	nonylbithiophene (4 isomers)	292
10C— (decylbithiophene structure)	decylbithiophene (3 isomers)	306
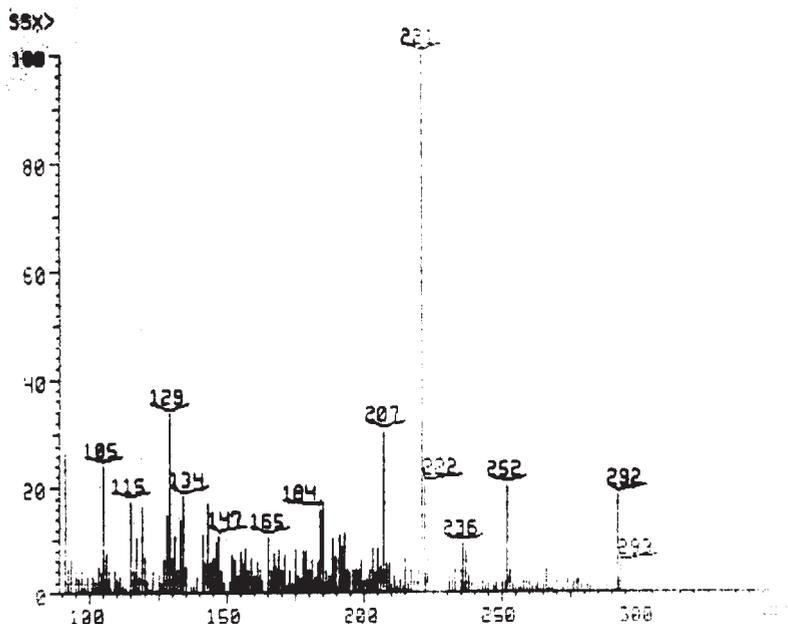
Figure 2. Mass spectra of nonylbithiophene in the SC3 subfraction of sample D1 (slightly overlapped with neighbouring compounds).

ence of 70 (292–222) is characteristic of the isoprenoid structure C_5, bonded on bithiophene skeleton.

Sulphur-containing compounds released in the pyrolysates (Figure 3, Table VI), comprise alkylthiophenes, alkenylthiophenes and benzothiophenes. Peak numbers in the chromatogram refer to the ordinal numbers of identified components listed in Table VI. Available reference organic sulphur compounds are marked by an asterisk in Table VI. The non-sulphur pyrolysis compounds are mainly alkanes and alkylbenzenes and their unsaturated analogues. The compounds identified are of the same type for all the three Dinaric samples examined and are the same as those found in the Vrelo outcrop,[15] which also represents an Upper Jurassic OSR sample collected on the surface of the Dinarides.
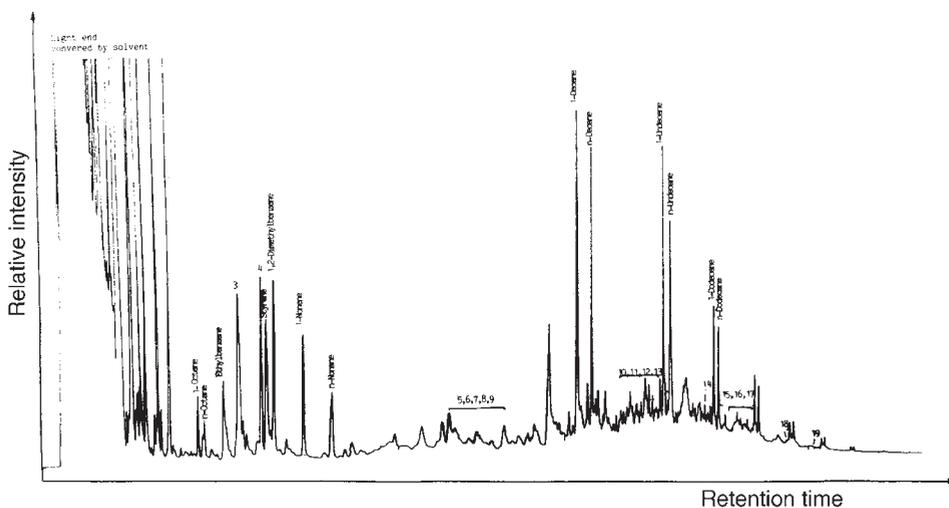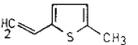

Figure 3. Gas chromatogram of the pyrolysis products of sample D1 in *n*-hexane.

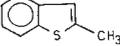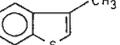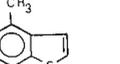According to Damste and coworkers,[9] thiophenes and benzothiophenes in pyrolysates show similar units in the kerogen. Thus, the similarity in the composition of sulphur-containing pyrolysis products might be taken as the reflection of kerogen structure similarity and their genetic relation.

The proportions of 2,3-dimethylthiophene, *n*-nonene and 1,2-dimethylbenzene, which serve for the classification of sulphur-containing kerogens,[10] classified the D1 and D2 kerogens into the same type (Type II-S), while the D3 kerogen is plotted outside the Type II-S area (Figure 4). However, D2 and D3 are closer to each other than D1 to D2 or D3. The S/C ratios deter-

TABLE VI

Sulphur-containing pyrolysis compounds obtained from kerogens

No.	Sulphur compound	Molecular mass
1	thiophene	84
2	methylthiophene	98
3	2,5-dimethylthiophene*	112
4	2,3-dimethylthiophene*	112
5	2,3,5-trimethylthiophene*	126
6	2-methyl-5-vinylthiophene	124
7	ethylmetylthiophene	126
8	1-propenylthiophene	124
9	2,3,4-trimethylthiophene*	126
10	2-ethyl-3,5-dimethylthiophene*	140
11	1-butenylthiophene	138
12	ethyldimethylthiophene	140
13	2,3,4,5-tetramethylthiophene*	140
14	benzo(b)thiophene	134
15	2-methylbenzo(b)thiophene	148
16	3-methylbenzo(b)thiophene	148
17	4-methylbenzo(b)thiophene	148
18	dimethylbenzo(b)thiophene	162
19	methylethylbenzo(b)thiophene	176
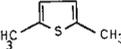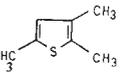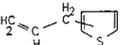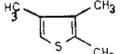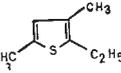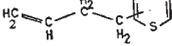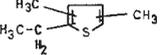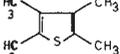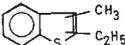
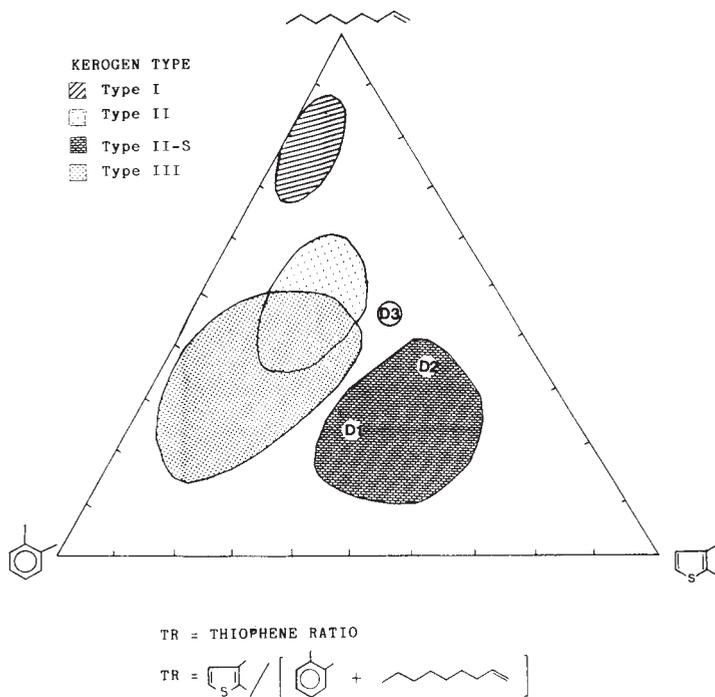* Components confirmed by reference compounds

Figure 4. Ternary plot showing the relative abundances of 2,3-dimethylthiophene, *n*-nonene and 1,2-dimethylbenzene (after Eglinton *et al.*[10]).

mined in all examined kerogens indicate II-S Type because S/C ratios are greater than 0.04.

CONCLUSION

The three Upper Jurassic OSR samples, taken from the surface of the Dinarides contain very high amounts of organo-sulphur compounds. By weight organically-bound sulphur makes up roughly a tenth of the kerogens and the bitumens. Pyrite and sulphate represent comperatively low percentages of sulphur (D1 and D2 are lower than D3), while elemental sulphur is negligible in all the samples studied.

In the subfractions: thiophenes, bithiophenes, thiolanes and benzothiophenes were identified and were found in all three samples. The compositions of organo-sulphur compounds identified point to a genetic relation of the investigated Upper Jurassic samples.

The compositions of alkylthiophenes, alkenylthiophenes and benzothio-phenes identified as pyrolysis products, are thought to reflect similar struc-ture units in their kerogens and are also the same for the Upper Jurassic OSR samples examined, indicatinga a genetic relationship.

The triangular distribution of 2,3-dimethylthiophene, *n*-nonene and 1,2-dimethylbenzene, as kerogen pyrolytic products, classifies samples D1 and D2 into the same type (Type II-S). Determined S/C ratio for D3 kerogen (0.055) indicates that it belongs to Type II-S also, though the D3 dot shows a deviation.

The very high organic sulphur and the very high TOC content show that the Upper Jurassic OSR which now outcrops on the surface of the Dinarides, was deposited most probably in an anoxic deposition environment which was poor in iron. The oil, (potentially) released from the OSR, should be expected to be very rich in organo-sulphur constituents.

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SAŽETAK

Raspodjela sumporovih spojeva u gornjojurskim naslagama Dinarida

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Ispitana je raspodjela elementarnog sumpora i sumpora vezanog u spojevima za tri površinska uzorka naftnomatične stijene gornjojurskih naslaga Dinarida.

Utvrđeno je da je u svakom od njih koncentracija elementarnog sumpora zanemariva, a koncentracija sumpora vezanog u pirit i sulfate niska. Nasuprot tome, udjel organski vezanog sumpora, kako u kerogenima tako i u bitumenima vrlo je visok i iznosi gotovo desetinu mase bitumena i mase kerogena.

U frakcijama bitumena metodom GC-MS identificirani su alkiltiofeni, alkilbitiofeni, alkiltiolani, alkilbenzotiofeni i alkildibenzotiofeni. Među produktima pirolize kerogena identificirani su alkiltiofeni, alkeniltiofeni i benzotiofeni.

Na temelju slične raspodjele sumpora i istovrsnosti organskih sumporovih spojeva u bitumenima i pirolizatima kerogena, te na temelju analognosti organskih sumporovih spojeva iz bitumena i pirolizata kerogena, ocjenjuje se da su ispitani uzorci geokemijski srodni.

Izrazito visoka koncentracija organske tvari kao i organski vezanog sumpora pokazuje da je okoliš taloženja gornjojurskih naslaga Dinarida bio najvjerojatnije gotovo bez kisika i siromašan ionima željeza.