

**TRACE ELEMENT DISTRIBUTIONS IN KEROGEN, BITUMENS AND PYROLYSATES
ISOLATED FROM NEW ALBANY SHALE**

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INTRODUCTION

Although trace element distributions have been used to correlate oils (1-8), there have been few similar studies on oil-source rock correlations (9).

The bitumen, kerogen or a pyrolysate from a source rock may, in principle, be used to correlate a source rock to an oil. However, if trace element abundances are to be used for oil-source rock correlations, the bitumen, kerogen and the pyrolysates of a source rock should show correlation in their trace element distributions. For example, it has been shown (10) that the kerogen of the New Albany shale releases Ni(II) and VO(II) porphyrins during pyrolysis in amounts that are directly proportional to organically combined Ni and V, in the kerogen.

In this study trace element distributions were measured in the bitumen and kerogen from the New Albany shale and in pyrolysates generated from the shale under different conditions (i.e., dry, hydrous, toluene, toluene/methanol). Trace element distributions were also compared in chromatographic fractions of the bitumen and pyrolysates. Implications for oil-source rock correlation are discussed.

EXPERIMENTAL

Detailed geological information on New Albany shale (Clark County, Indiana) are reported elsewhere (11). The procedures for the extraction of the bitumen I and II and the isolation of kerogen by demineralization were similar to those of Mercer *et al.* (12). Boscan (Venezuela) crude oil was also analyzed for comparison.

Shale samples (150 g) were pyrolysed for 5 hours at 300°C in a 1L autoclave in toluene, toluene/methanol (7:3), or water (200 mL each) and without solvent ("dry" conditions) at initially 1 atm N₂. The pyrolysed shale samples were extracted as for the bitumen-I. The shale which was pyrolysed in toluene was re-pyrolysed four times in toluene and for a fifth time in toluene/methanol (7:3) under the same conditions.

Liquid chromatography (silica gel) was used to separate the bitumen and pyrolysate samples into fractions for analysis. The first fractions were eluted with a) hexanes (saturates), b) CH₂Cl₂ in hexanes (porphyrin aggregate), c) CHCl₃ (polar material), and d) 7:3 toluene/methanol followed by 100% methanol (asphaltenes plus other highly polar fractions).

Trace element concentrations were determined by instrumental neutron activation analysis (INAA) using the method published previously (12,13).

RESULTS

The concentrations of 13 elements in New Albany bitumens, kerogen and pyrolysates are listed in Tables 1 and 2.

The kerogen is the source of Ni and V complexes found in the pyrolysates (10) and, through maturation, of the complexes in the bitumen I and II. Hence, it might be expected that the pyrolysates should have similar Ni/V ratios as the kerogen (1.91 after accounting for inorganic Ni contributions, 12). The first toluene pyrolysate, however, has a Ni/V ratio similar to that of the bitumen-I (0.91 and 0.95, respectively) rather than that of the kerogen (1.91). Subsequent toluene pyrolysates, as well as the hydrous, dry, and toluene-methanol pyrolysates, have Ni/V ratios which are similar to that of the kerogen. Thus the first toluene pyrolysate may represent residual bitumen I but the subsequent pyrolysates reflect the Ni/V ratio of the kerogen. Previous electron microprobe work with the New Albany shale (14) indicates that the kerogen is intimately associated with the clay minerals present in the rock. Hence, the extraction of the bitumen-I by sonication in a solvent at 40°C is probably incomplete. Thus, the first heating in the presence of toluene may generate a pyrolysate which is predominantly an improved extraction of the remaining inherent bitumen in the bitumen-I extracted shale, while the subsequent pyrolysates are generated primarily from the breakdown of kerogen. A similar conclusion was reached by Van Berkel, et al (15) to explain the similarity of an initial toluene pyrolysate of the New Albany kerogen and the bitumen-II extracted from the kerogen.

The data in Tables 1 and 2 show that the solvent plays a role in determining the resultant Ni/V ratio of the pyrolysate. Variations of the Ni/V ratio are probably related to the composition of the pyrolysate (i.e., polar versus nonpolar material) which is dependent on the polarity of the solvent and possibly to solvent-mineral interactions. The composition of the bitumen-I and the pyrolysates can be compared using the relative abundances of nonpolar (fractions 1 plus 2) and polar material (fractions 3 plus 4) measured by the chromatographic separation. Table 3 shows the Ni/V values compared to the non-polar/polar ratio. The hydrous and toluene/methanol pyrolysates contain the highest proportion of asphaltic/polar material and have Ni/V ratios very similar to that of the kerogen. A possible explanation is that water and methanol (in the toluene/methanol pyrolysis) deactivate the clay mineral-bitumen-kerogen interface, thus reducing conversion of asphaltic material to nonpolar hydrocarbons. Similarly, Ni and V complexes released by the kerogen are poorly adsorbed by the deactivated mineral matrix and thus the Ni/V ratios are similar to that of the kerogen. The higher Ni/V ratio (relative to the hydrous and toluene/methanol pyrolysates and the kerogen) observed for the dry pyrolysate is probably due to the high yield of the nonpolar fraction resulting from catalytic action of the clays. The large amounts of nonpolar organic matter generated during pyrolysis may

act as a nonpolar solvent and preferentially extract more of the less-polar Ni(II) porphyrins than the polar VO(II) species, thereby producing a pyrolysate with a higher Ni/V ratio than that of the hydrous or toluene/methanol pyrolysates. Similarly, under non-hydrous conditions the active clay surfaces retain the more polar VO(II) species relative to the less polar Ni(II) species. The second and third toluene pyrolysates were also likely to be derived from the breakdown of kerogen in which the catalytic action of the clays is not inhibited, such that conditions are similar to those of the dry pyrolysis.

For elements other than Ni and V the data in Tables 1 and 2 indicate that considerable variations in concentration relative to the bitumen I are observed. None of the pyrolysis conditions produces a pyrolysate that contains trace element distributions identical to that of the bitumen I; the hydrous pyrolysate is closest.

Distribution of Trace Elements in Pyrolysate Fractions. The four chromatographic fractions of each pyrolysate and the bitumen I were analyzed for trace elements. Distributions of trace elements among these fractions (i.e., percentage of element in each fraction relative to original sample) were similar for all pyrolysates and the bitumen I. Data for Ni, V, Se, Cr, Co, Fe and As in the bitumen I and the hydrous pyrolysate are shown in Figure 1. Figure 1 shows that Ni, V, and Se (Fig. 1a,b) are distributed differently from Cr, Cu, Fe, and As (Fig. 1c,d). Data for Ga, Mo, Sb, Zn, and Mn show similar patterns to Cr, Fe, Co and As. Nickel and vanadium are present predominantly as metalloporphyrins in the bitumen and the hydrous pyrolysate (porphyrin aggregate plus the CHCl_3 fraction which contains Ni(II) and VO(II) porphyrins). Only minor amounts of Ni and V are present in the asphaltene-polar fraction (<17%) and part of this is probably porphyrinic because weak Soret peaks at 390-410 nm are observed in this fraction. Hence, greater than 80% of the Ni and V in the bitumen and in the hydrous pyrolysates is present as metalloporphyrins. The distribution of Se in the bitumen I and the hydrous pyrolysate is related to that of sulfur. The non-polar (hexanes) fraction contains elemental sulfur and analysis of this fraction of the bitumen-II shows that approximately 86% of the sample was elemental sulfur. The mass spectrum of some of the sulfur crystals (Figure 2) revealed that the sulfur occurs predominantly as S_8 and that Se substitutes for a S in the S_8 ring to give the S_7Se molecule. Therefore, the Se observed in the nonpolar fractions of the pyrolysates is associated with elemental sulfur. The elemental sulfur is probably formed by the breakdown of sulfides, primarily pyrite and marcasite (FeS_2), during pyrolysis. The data also suggests that there is a considerable amount of elemental S/Se in the bitumen-I. This "inherent" elemental sulfur could be derived from weathering, bacterial activity or exposure to any other conditions which are capable of oxidizing sulfide minerals and could have occurred at any point in the history of the rock.

The distributions of Cr, Co, Fe and As (and other elements not shown in Fig. 1) in the hydrous pyrolysate and the bitumen I are similar. These elements are concentrated in the polar fraction (asphaltenes) although mass balance calculations show some retention of the column of these elements, presumably associated with highly polar asphaltenes that did not elute.

The similarity in trace element distributions in the chromatographic fractions of the bitumen I and the hydrous pyrolysate (and other pyrolysates) of the shale indicate that metal species or complexes generated by the kerogen by maturation in the bitumen I and by pyrolysis are also similar. Differences in absolute concentrations among the pyrolysates and the bitumen are probably due to kerogen-mineral or metal species-mineral interactions during interaction of pyrolysis.

CONCLUSION

1. The trace element concentrations in the pyrolysates vary significantly. It is necessary, therefore, to be consistent when choosing pyrolysis conditions for comparative purposes or for correlation work. Hydrous pyrolysis appears to give trace element concentrations closest to those of the bitumen I.
2. The Ni/V ratios observed for the pyrolysates are significantly different from that of the bitumen-I, except for the first toluene pyrolysate which may be residual bitumen-I released during initial pyrolysis. Excluding the first toluene pyrolysate, the Ni/V ratio of the pyrolysates resembled that of the kerogen. The major factor controlling the Ni/V ratio in the pyrolysates appears to be the polarity of the pyrolysis solvent and its deactivating effect on clay catalysis and related adsorption of metal species on clays. Deactivation of clay surfaces by water or methanol (hydrous or toluene/methanol pyrolysis) results in a pyrolysate with a higher proportion of polar material and Ni/V ratios similar to that of the kerogen. Pyrolysis under dry conditions or in toluene (pyrolysates 2 and 3) results in higher proportions of nonpolar material and pyrolysates have higher Ni/V ratios than those generated under hydrous or toluene/methanol conditions.
3. The elemental S and Se in the bitumen II result from decomposition of sulfides (FeS_2) during demineralization and are present primarily as S_8 and S_2Se which elute in the nonpolar fraction. Thus, the S and/or Se content of the nonpolar fraction of pyrolysates may be related to the amount of sulfide mineral breakdown during pyrolysis.

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Table 1. Concentrations of trace elements in the kerogen, bitumens and pyrolysates of the New Albany shale and in Boscan crude oil.

Element	Elemental Concentration ($\mu\text{g/g}$)							
	Kerogen ¹	Bitumen I	Bitumen II	Dry Pyr.	H ₂ O Pyr.	Toluene Pyr.	Tol/MeOH Pyr.	Boscan Crude
As	36.4	75.8	89.1	86.3	64.5	536	406	0.320
Co	115	8.63	113	14.3	10.6	13.4	61.2	0.224
Cr	35.2	1.04	12.3	1.75	0.865	1.65	1.39	0.401
Fe	0 by defn.	353	3140	556	744	992	1180	15.9
Ga	11.0	7.93	32.6	2.30	4.77	6.78	7.12	0.147
Mn	0	0.32	1.24	0.62	0.43	0.53	0.59	0.109
Mo	2400	28.7	460	17.4	6.24	54.6	29.8	4.26
Na	1240	156	816	8.57	1.71	53.0	53.7	25.0
Ni	2160	2560	3710	896	2760	1710	2300	97.2
Sb	72.6	0.598	56.0	12.2	0.561	1.40	1.38	0.296
Se	175	79.5	3840	18.9	215	43.8	7.86	0.320
V	1130	2700	3400	365	1540	1880	1230	1200
Zn	71.9	65.7	252	10.5	66.5	53.6	67.3	0.608
Ni/V	1.91	0.95	1.09	2.45	1.80	0.91	1.87	0.081
Ratio	± 0.25	± 0.02	± 0.03	± 0.17	± 0.06	± 0.03	± 0.13	± 0.006
Yield (%)	25%	1.4%	0.37%	3.6%	1.0%	1.0%	1.5%	--

¹ Corrected for inorganic contributions by the density fraction method described by Mercer *et al.* (22).

Table 2. Concentrations of trace elements in the sequential pyrolysates and residual bitumen (bitumen-III) from the pyrolyzed New Albany shale.

Element	Elemental Concentration ($\mu\text{g/g}$)							
	Pyr. #1	Pyr. #2	Pyr. #3	Pyr. #4	Pyr. #5	Pyr. #6	Bitumen III	
As	536	85.1	80.0	290	77.7	8.74	118	
Co	13.4	7.04	4.81	3.30	0.360	0.834	7.13	
Cr	1.65	2.50	0.786	1.41	0.770	0.50	6.82	
Fe	992	594	389	395	151	65.5	1405	
Ga	6.78	2.77	2.65	5.87	0.815	0.579	21.6	
Mn	0.53	1.18	0.380	0.566	0.42	0.48	0.61	
Mo	54.6	17.3	25.9	45.3	17.6	14.1	344	
Na	53.0	230	50.0	70.0	45.3	86.0	18.6	
Ni	1713	1189	933	777	276	458	516	
Sb	1.40	0.267	0.960	0.545	0.17	0.135	15.6	
Se	43.8	80.1	51.1	169	131	18.0	956	
V	1883	484	393	471	126	242	384	
Zn	53.6	12.2	7.03	13.0	7.31	37.0	52.1	
Ni/V	0.91	2.46	2.37	1.65	2.19	1.89	1.34	
Ratio	± 0.03	± 0.06	± 0.10	± 0.10	± 0.11	± 0.92	± 0.07	
Yield (%)	1.0	0.54	1.3	0.29	0.16	0.22	0.33	

¹ Pyrolysis runs 1-5 in toluene, run 6 in toluene/MeOH

² Bitumen-III = extractable organic material of shale after six pyrolyses and desmineralization.

Table 3. Ni/V and Non-Polar/Polar Ratios.

Sample	Ni/V	Non-Polar/Polar*
Kerogen	1.91	--
Bitumen I	0.95	1.04
Toluene Pyr. 1	0.91	0.94
Toluene Pyr. 2	2.46	1.54
Toluene Pyr. 3	2.37	1.81
Dry Pyr.	2.45	1.64
Hydrous Pyr.	1.80	0.65
Toluene/MeOH Pyr	1.87	0.68

* Computed from fractional yields of fractions (1+2)/(3+4).

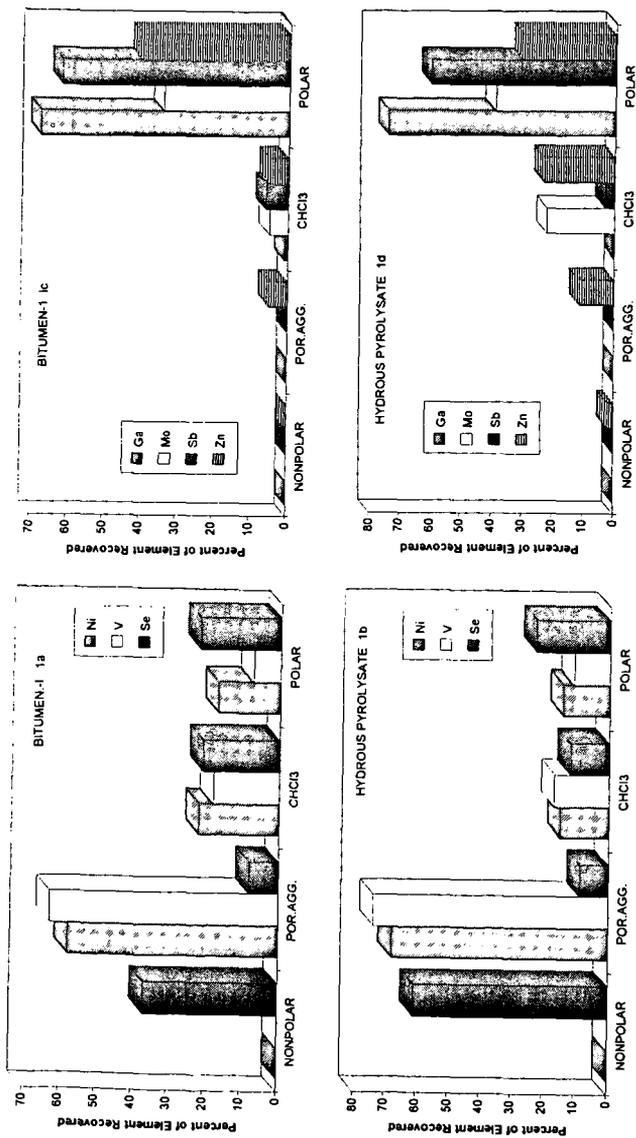


Figure 1: Comparison of elemental distributions in the bitumen I (a,c) and the hydroxy pyrolysate (b,d)

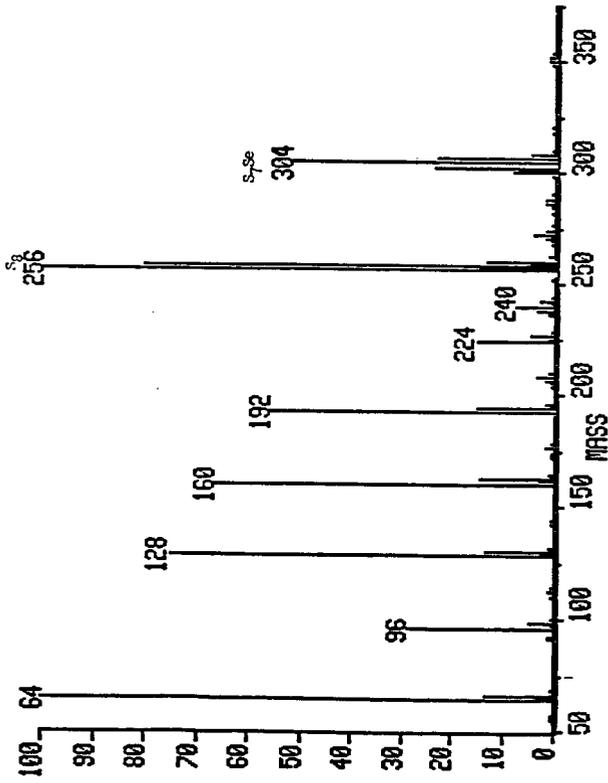


Figure 2: EIMS spectrum of the non-polar fraction of the bitumen II of the Albany Shale