

**THE EFFECT OF MINERALS ON TRACE ELEMENT DISTRIBUTIONS IN  
HYDROUS PYROLYSATES OF KEROGENS FROM THE NEW ALBANY SHALE**

S. L. Fitzgerald and R. H. Filby  
Department of Chemistry  
Washington State University  
Pullman, WA 99164-4630

**Keywords:** Minerals, Trace Elements, Pyrolysis

**INTRODUCTION**

Trace element complexes are present in most crude oils and source rock bitumens (1). Past studies have used trace element distributions in oil-oil (2-10) and to a lesser extent in oil-source rock correlation studies (11,12). Unfortunately, the use of trace element distributions in correlation studies is limited because, other than the nickel and vanadyl porphyrins, very little is known about the nature of these trace element complexes. Even less is known about the parameters controlling their distributions in oils and bitumens (1).

Mineral matter has been shown to play an important role during the catalytic alteration of kerogen to form petroleum (13-18). Kaplan and co-workers (13-15) demonstrated that, during kerogen pyrolysis, the presence of clays decreases the pyrolysate yield due to adsorption of polar constituents and the increase in gaseous products. Work by Rose et. al (19) also showed that while the addition of minerals did not increase the aromatization of the kerogen, they did alter the pyrolysate yields.

Considering the effect that minerals in the source rock have on the hydrocarbon distributions during petroleum formation, it seems reasonable that they also influence the trace element contents in crude oils. In order to study this influence, kerogen from the New Albany shale was subjected to hydrous pyrolysis in the presence and absence of added minerals. A comparison of the trace element abundances in the generated pyrolysates and in the whole shale bitumen indicates the extent to which minerals control the trace element contents in the New Albany bitumen.

**EXPERIMENTAL**

Kerogens were isolated from the New Albany shale as described previously (20). The bitumen-II was removed from the kerogen by soxhlet extraction (48 hrs.) using chloroform,

the kerogen was then separated into float/sink fractions by suspension in chloroform to remove residual minerals (mostly pyrite). The minerals added in the pyrolysis experiments were calcite, pyrite, Na-montmorillonite, kaolinite, and illite.

In a typical experiment, 30g of kerogen and 30g of mineral were mixed in a Pyrex "sleeve" with 130 mL deionized water. The "sleeve" was then placed in a 1L autoclave. The system was flushed with nitrogen, and heated for 5 hours at 300°C. Temperatures were monitored through a thermo-well placed directly into the sample. For comparative purposes, the bitumen-I extracted shale was pyrolysed under hydrous conditions (150g shale, 200 ml H<sub>2</sub>O) for 5 hrs. at 300°C.

The pyrolysates were recovered after each pyrolysis by the same extraction method used to recover the bitumen-II. Pyrolysate yields were determined relative to the amount of kerogen originally pyrolysed and were not corrected for mineral content, mechanical sample loss, or losses due to formation of gaseous products. Trace element concentrations for all samples were determined by instrumental neutron activation analysis (INAA) using the method described previously (21).

## RESULTS AND DISCUSSION

Pyrolysate yields. The pyrolysis of kerogen with calcite gave the lowest yield of all the runs (table 1). This is consistent with the observations of Huizinga et. al. (15) who noted (for short heating times) lower pyrolysate yields for kerogens with calcite during both dry (and to a lesser degree) hydrous pyrolysis. They attributed this decrease in yield to inefficient heating due to the large amount of mineral present. It seems more likely that this effect is the result of an interaction between the kerogen and the calcite, however, since similar results were obtained under the conditions of this study (i.e. lower kerogen to mineral ratio, hydrous conditions, and temperature measured from within the sample).

The decrease in pyrolysate products generated in the presence of montmorillonite, and illite also agreed with the findings of Huizinga et. al. (15). They demonstrated that these clays have high adsorptive capacities for the more polar components of the pyrolysate, and thermocatalytically induce the formation of more gaseous products. These two effects cause a net reduction in pyrolysate yield. In contrast, however, the kerogen heated with kaolinite gave an increase in yield. This seems to indicate that kaolinite provides some thermocatalytic activity with a substantially lower adsorption capacity for pyrolysate products than illite or montmorillonite.

Trace Elements. The concentrations of twenty trace elements in the bitumens, kerogen, and related pyrolysates are

shown in Table 1. For the sake of brevity only the nickel and vanadium values and their ratios will be discussed here. As can be seen from the graph in Figure 1, the vanadium concentrations for the different kerogen pyrolysates are fairly constant. This indicates that the minerals used have very little if any effect on the abundance of vanadyl porphyrins in the pyrolysates. The nickel concentrations (Fig. 2), however, show substantial variation among the pyrolysates. The most noticeable trend is the increase in nickel concentrations from Na-montmorillonite to kaolinite to illite. One explanation for this trend could be the preferential adsorption of nickel porphyrin with montmorillonite being the strongest adsorbent and illite the weakest. However, this is inconsistent with the pyrolysis yield data which indicates that kaolinite is the least adsorbent of the three clays. Another explanation for this trend is that the clays are causing the preferential decomposition of the nickel porphyrins on the surface as a function of surface acidity (Na-montmorillonite being the most acidic).

The value for the nickel concentration from the kerogen-pyrite (KP) pyrolysis shows a dramatic drop which is comparable to the concentration from the montmorillonite run. It has been shown that at temperatures above 240 C, porphyrins in the presence of H<sub>2</sub>S are partially decomposed. Also in the presence of H<sub>2</sub>S and a Co-Mo catalyst, nickel and vanadyl porphyrins can be demetallated with nickel porphyrins having the higher demetallation rate (22). The generation of large amounts of H<sub>2</sub>S during pyrolysis with pyrite could possibly explain the observed drop in the nickel concentration. The pyrolysis with calcite also shows a drop in nickel concentration similar to the value seen in the kaolinite run. It is uncertain at this time why calcite would have this effect on the nickel porphyrins and further investigation is needed to determine the cause of this effect.

A comparison of the Ni/V ratios for the bitumens, kerogen, and related pyrolysates is shown in Figure 3. It can be seen from this comparison that the Ni/V ratios are similar for the kerogen, and for the pyrolysates from the original kerogen, the kerogen float, and the whole shale. This is unsurprising since the kerogen is the source of the Ni and V complexes in these pyrolysates. Variations in the Ni/V ratio in pyrolysates generated in the presence of minerals reflect the variations in the nickel concentrations for the pyrolysates.

A comparison of the bitumen-II Ni/V ratio with that from the Na-montmorillonite pyrolysate shows the two have very similar values. This indicates that the Ni porphyrin in the bitumen-II, which is more intimately associated with the mineral component of the shale, may be decomposing due to interaction with clays.

## CONCLUSIONS

The work presented here indicates that the mineral matrix of the shale plays an important role in determining the trace element distributions during petroleum formation. The data show variations in the Ni during pyrolysis of kerogen with clays and pyrite, whereas the V concentration remains essentially constant. Further investigation is needed to determine if this loss is due to the adsorption or the decomposition of the nickel complexes present.

## ACKNOWLEDGMENTS

The authors thank Cathy Grimm and the Nuclear Radiation Center staff for their prompt aid during the instrumental neutron activation analysis.

## REFERENCES

1. Branthaver, J.F. and Filby, R.H., in "Metal Complexes In Fossil Fuels", eds. Filby, R.H. and Branthaver, J.F., ACS Symposium Series No. 344, American Chemical Society: Washington, DC, 1987.
2. Hodgson, G.W., *Bull. Am. Assoc. petrol. geol.*, 1954, **38**, 2737-54.
3. Hodgson, G.W., Fiores, J., Baker, B.L. *Bull. Am. Assoc. Petrol. Geol.* 1959, **43**, 311-28.
4. Hitchon, B., Filby, R.H. *Alberta Research Council Open File Report* 1983-02, 144 p.
5. Hitchon, B., Filby, R.H. *Bull. Am. Assoc. Petrol. Geol.* 1984, **68**, 838-49.
6. Hyden, H.J., *U.S. Geol. Serv. Bull.* 1100-B, 1961.
7. Saban, M., Vitorovic, O. and Vitorovic, in "Symposium on Characterization of Heavy Crude Oils and Petroleum Residues", Editions Technip: Paris, 1984.
8. Al-Shahristani, H. and Al-Atyia, M.J., *Geochim. Et Cosmochim. Acta*, 1972, **36**, 929-37.
9. Curiale, J.A. In "Exploration for Heavy Oil and Bitumen"; Am. Assoc. Petrol. Geol. Research Conference, Santa Maria, Calif., Oct. 28-Nov. 2, 1984, Vol.1, pp.1-39.
10. Curiale, J.A., in "Metal Complexes in Fossil Fuels", eds. Filby, R.H. and Branthaver, J.F., ACS Symposium Series No. 344, American Chemical Society: Washington, DC, 1987.
11. Hirner, A.V., in "Metal Complexes in Fossil Fuels", eds. Filby, R.H. and Branthaver, J.F., ACS Symposium Series No. 344, American Chemical Society: Washington, DC, 1987.
12. Chakhmachkev, V.A., Lositskaya, I.F., Punanova, S.A., Semenova, R.A. *Geokhimiya* 1985, 703-09.

13. Lu, S.-T., Kaplan, I.R. *Geochim. et Cosmochim. Acta*, 1985, **49**, 2589-2604.
14. Tannenbaum, E., Huizinga, B.J. and Kaplan, I.R. *Amer. Assoc. Petrol. Geol. Bull.*, 1986, **70**, 1156-1165.
15. Huizinga, B.J., Tannenbaum, E. and Kaplan, I.R. *Org. Geochem.*, 1987, **11**, 591-604.
16. Lu, S.-T., Ruth, E. and Kaplan, I.R. *Org. Geochem.*, 1989, **14**, 491-499.
17. Lu, S.-T. and Kaplan, I.R. *Org. Geochem.*, 1989, **14**, 501-510.
18. Espitalie, J., Makadi, K.S. and Trickett, J. *Org. Geochem.*, 1984, **6**, 365.
19. Rose, H.R., Smith, D.R., Hanna, J.B., Palmisano, A.J. and Wilson, M.A. *Fuel*, 1992, **71**, 355-360.
20. Mercer, G.E., Fitzgerald, S.L., Day, J.W. and Filby, R.H. *ACS Fuel Div. Preprints*, 1991, **36**, 1180-1189.
21. VanBerkel, G.J., Ph.D. Thesis, Department of Chemistry, Washington State University, 1987.
22. Rankel, L.A. *Preprints Div. Petrol. Chem. ACS*, 1981, **26**, 689.

Table 1. Trace element concentrations in kerogen pyrolysates (WK-KL), bitumens (Bl, Bll), shale pyrolysate (SP), and kerogen (KER).

|                  | WK    | K     | KP    | KC    | KM    | KK    | KL    | Bl    | SP     | Bll   | KER   |
|------------------|-------|-------|-------|-------|-------|-------|-------|-------|--------|-------|-------|
| As (ppm)         | 18.1  | 3.07  | 32.0  | 1.54  | 1.76  | 4.33  | 3.24  | 1.78  | 4.36   | 120   | 89    |
| Br (ppm)         | 14.0  | 17.6  | 14.6  | 12.0  | 6.73  | 12.1  | 10.1  | 12.1  | 30.6   | 102   | 12.6  |
| Cl (ppm)         | 5920  | 12600 | 6210  | 6230  | 2200  | 9640  | 2620  | 617   | 1680   | 13900 | 59100 |
| Co (ppm)         | 26.2  | 2.24  | 2.08  | 10.6  | 1.50  | 1.18  | 1.48  | 4.46  | 64.6   | 17.7  | 67.0  |
| Cr (ppm)         | 22.2  | 34.5  | 95.0  | 0.866 | 0.396 | 21.4  | 2.28  | 0.794 | <0.516 | 1.29  | 35.8  |
| Cu (ppm)         | 232   | 269   | 422   | <27.9 | <35.9 | 96.6  | 53.3  | <68.7 | <71.3  | 308   | <1070 |
| Fe (ppm)         | 237   | 566   | 121   | 892   | 26.0  | 566   | 130   | 152   | 492    | 1600  | 33800 |
| Ga (ppm)         | 31.5  | 20.5  | 13.2  | 4.43  | 4.40  | 15.8  | 23.6  | 0.498 | 2.82   | 14.4  | 27.6  |
| Hg (ppm)         | 7.64  | 9.58  | 15.0  | 193   | 18.6  | 9.44  | 12.0  | 93.6  | 20.6   | 370   | 33.8  |
| La (ppb)         | 496   | 254   | 193   | 104   | 60.3  | 130   | 432   | 38.4  | <57.6  | 214   | 33000 |
| Mn (ppb)         | 243   | 337   | 620   | 356   | 194   | 330   | 273   | 529   | 1180   | 602   | 27700 |
| Mo (ppm)         | 4.79  | 7.94  | 7.26  | 1.27  | 1.46  | 5.47  | 3.98  | 4.35  | 3.72   | 101   | 1230  |
| Na (ppm)         | 29.7  | 23.2  | 157   | 34.8  | 30.1  | 13.6  | 20.8  | 31.4  | 25.6   | 36.0  | 3280  |
| Ni (ppm)         | 3290  | 2600  | 1560  | 1940  | 1600  | 1920  | 2700  | 2180  | 3460   | 2405  | 1630  |
| Sb (ppb)         | 749   | 348   | 330   | 130   | 90.5  | 376   | 170   | <89.4 | 130    | 23100 | 26000 |
| Sc (ppb)         | 3.11  | 2.12  | 19.7  | 3.38  | 1.81  | 2.66  | <3.74 | 1.68  | 6.14   | 23100 | 26000 |
| Se (ppm)         | 32.2  | 33.1  | 62.2  | 20.9  | 77.8  | 39.2  | 50.8  | 373   | 82.2   | 1510  | 4190  |
| Th (ppb)         | 24.6  | <28.3 | <32.6 | <31.8 | <23.3 | <27.5 | 24.4  | <35.6 | 65.6   | <105  | 136   |
| V (ppm)          | 1430  | 1120  | 1040  | 1040  | 1200  | 1050  | 1160  | 2540  | 1590   | 2070  | 3560  |
| Zn (ppm)         | 36.6  | 24.0  | 274   | 20.3  | 2.95  | 14.4  | 9.10  | 11.0  | 56.6   | 61.8  | 741   |
| NiV              | 2.30  | 2.32  | 1.50  | 1.87  | 1.33  | 1.83  | 2.33  | 0.86  | 2.22   | 1.16  | 2.47  |
| Pyrolysate Yield | 3.97% | 4.84% | 3.40% | 2.87% | 3.04% | 5.59% | 3.38% | n/a   | 0.97%  | n/a   | n/a   |

WK=untreated kerogen, K=kerogen total, KP=kerogen-pyrite, KC=kerogen-carbitol, KM=kerogen-montmorillonite  
 KK=kerogen-kaolinite, KL=kerogen-illite, Bl=bitumen I, SP=extracted shale pyrolysate, Bll=bitumen II, KER=kerogen  
 \*Percentages refer to original kerogen mass (not corrected for mineral content), except for NAP which refers to extracted shale mass.

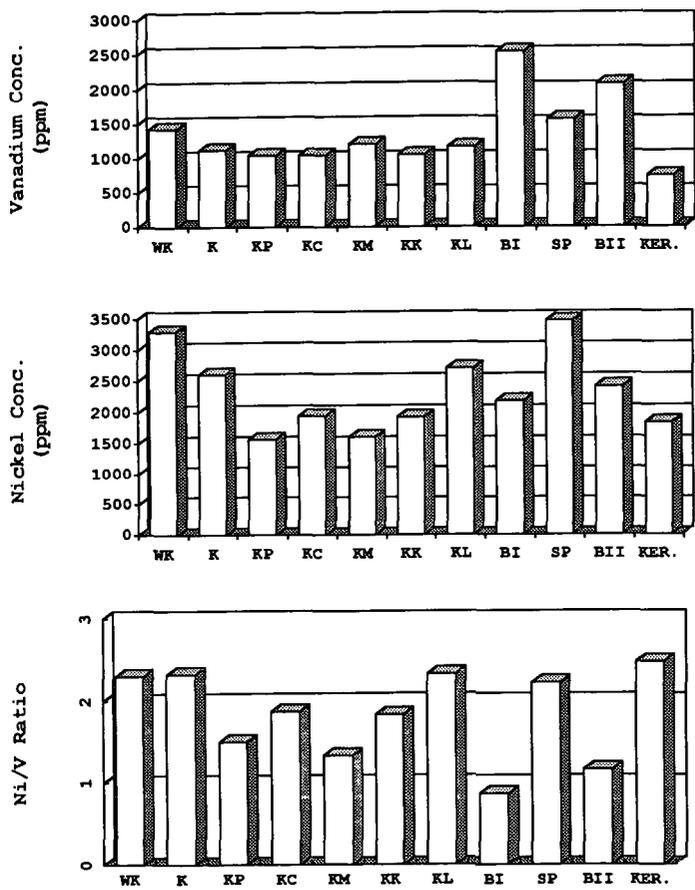


Figure 1 (upper); 2 (middle); 3 (lower) Vanadium, Nickel, and Nickel/Vanadium Ratios in New Albany Kerogen Pyrolysates.

WK=untreated kerogen, K=kerogen float, KP=kerogen+pyrite, KC=kerogen+calcite, KM=kerogen+montmorillonite, KK=kerogen+kaolinite, KL=kerogen+illite, BI=bitumen I, SP=extracted shale pyrolysate, BII=bitumen II, KER.=kerogen