DETERMINATION OF ORGANIC/INORGANIC ASSOCIATIONS OF TRACE ELEMENTS IN AN OIL SHALE KEROGEN

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INTRODUCTION

The distributions of trace element in crude oils have been used to classify crude oils into families (1-4). Relatively little work, however, has been performed using trace element abundances for oil-source rock correlations. One reason for the paucity of oil-source rock correlations using trace elements is the difficulty in obtaining accurate trace element data for the organic matter (bitumen and kerogen) found in source rocks. The most difficult problem is the determination of trace element abundances in kerogens which are the precursors to crude oils. The chemical species of metals present in kerogens must be known to provide the relationship between such species and the metal complexes in crude oils. Difficulties in kerogen analysis arise primarily from the method of isolation, i.e., dissolution of the mineral matrix of the rock. In the conventional method of isolation the mineral matrix is dissolved in HCl/HF. This leaves a kerogen containing HCl/HF resistant minerals and neoformed fluorides. Several methods to remove or account for these inorganic contributions to the kerogen composition have been proposed, and include low temperature ashing (LTA) (5), density separations (6) and chemical removal of residual mineral matter (7-9). Although most of these methods improve trace element data, they have drawbacks; for example, density separations are usually incomplete (7) and chemical removal techniques do not dissolve the major resistant minerals without seriously altering the organic matter. The LTA method which is based on low temperature oxidation of organic matter to CO_2 + H_2O and conversion of organically combined metals to acid-soluble oxides is affected by the presence of neoformed fluorides and by partial oxidation of pyrite/marcasite (11).

This paper compares two methods of determining inorganic/organic trace element abundances in kerogen with the LTA method developed previously (11). A combination of INAA with X-ray diffraction analysis and analysis of mineral grains by electron microprobe (EMP-XRF) was used to analyze density fractions of the New Albany Shale kerogen and a mineral-rich fraction of the kerogen. The New Albany kerogen was chosen because of the large Ni and V concentrations and because of the high metalloporphyrin concentrations in the shale (12).

EXPERIMENTAL

1. Kerogen Isolation. Mississippian New Albany shale (Henryville Bed Clark County, IN) was ground to ~200 mesh in a ring mill, washed with distilled water and vacuum dried at 65°C. Resultant shale samples were extracted with toluene-methanol (7:3) to remove bitumen and demineralized as indicated in Figure 1. Detailed geological information on New Albany shale may be found elsewhere (10).

2. Density Separations. A kerogen sample isolated using the scheme shown in Figure 1 were subjected to a density fractionation using chloroform. In this separation the kerogen was sonicated in chloroform at 40°C for an hour and centrifuged. Roughly 80% of the kerogen was recovered in a float fraction, 15% as a sink fraction and ca. 1% as a mineral residue which was approximately 85% pyrite and marcasite. A portion of the mineral residue was treated with 3M nitric acid at 45°C for one hour to remove the pyrite and marcasite from minor mineral components, (e.g., rutile, chalcopyrite, anatase, etc.).

3. Instrumental Neutron Activation Analysis (INAA). All samples were analyzed for trace element contents by INAA using a method similar to that of Jacobs and Filby (13).

4. X-ray Diffraction (XRD). the major mineral composition of the samples was determined by XRD using a Siemens x-ray diffractometer. Appropriate portions of each powdered sample were smeared on a glass slide and diffraction patterns measured using the Cu-K_α line.

5. Electron Microprobe X-ray Fluorescence (EMP-XRF). Trace element associations with individual mineral grains within the kerogen were determined by EMP-XRF. Electron dot maps of several elements in ashed kerogen were made using a Cameca electron microprobe. The microprobe was also used in the SEM mode to obtain electron micrographs of the mapped mineral grins. For both electron dot maps and micrographs an electron accelerating voltage of 20keV was used. Concentrations of several elements in individual mineral grains were also determined.

6. Low Temperature Ashing (LTA). Kerogen samples were ashed using a LFE Model LTA-302 low temperature asher operated at 50 RF watts and an O_2 flow rate of 2 mL/min. Ashed samples were treated with 2M HCl and heated to 40°C with constant stirring for one hour to remove metal oxides formed in the ashing process. The acid-leached ash was isolated by centrifugation.

RESULTS AND DISCUSSION

1. X-ray Diffraction Results

The major minerals identified by XRD in New Albany kerogen were pyrite and marcasite. Additional minor mineral components were identified by ashing the kerogen followed by removal of the pyrite and marcasite from the mineral residue with 3M HNO_3. In the ashed kerogen ralstonite ($NaMgAl(F,OH)_6.nH_2O$) was identified. This mineral is an artifact of the kerogen isolation procedure as discussed elsewhere (5,11). Leaching of the ash with 3M HNO_3 removed ralstonite, pyrite and marcasite and XRD identified anatase, rutile and chalcopyrite ($CuFeS_2$). With these inorganic contributions revealed, correction methods were focused on the minerals identified above.

2. Fractionation of Kerogen by Density: Determination of Concentrations in Inorganic and Organic Components.

The concentrations of trace elements determined by INAA for the kerogen and its density fractions are listed in Table 1. A number

of general conclusions concerning the inorganic/organic nature of trace elements in the kerogen may be drawn from the data. Elements which tend to concentrate in the float fraction (Ni, V, Mo, Sb) probably have high organic associations. Similarly, elements concentrating in the most dense fraction, the mineral residue (As, Cr, Fe, Hf, Mn, Ti, Zr) most likely are present predominantly in mineral form. The elements which concentrate in the intermediate density sink fraction (Al, Mg, Na, Cs, Rb, Sc) appear to be associated with neoformed fluorides, such as ralstonite. However, some elements show no appreciable concentration in any fraction (Co, Se) and possibly exist in both inorganic and organic forms in the kerogen.

A method to determine the concentrations of the elements in the "organic" and "inorganic" compounds was formulated based upon the weight fractions of the organic and inorganic components. In this method the following assumptions are made:

1) The mineral matter and organic matter are similar in the float and sink fractions. The fractions differ only in the relative amounts of organic and mineral matter.

2) The concentration of V in organic combination is very large relative to the V in inorganic combination.

3) The concentration of Fe in inorganic combination is very large relative to the Fe in organic combination.

Using these assumptions, the inorganic and organic weight fractions for the sink and float kerogen samples were determined as shown in Figure 2. Once the weight fractions (f_{1O}, f_{1m}; f_{2O}, f_{2m}) are known, the concentration of any element may be determined for both the organic and inorganic components of kerogen by solving the two simultaneous equations shown at the bottom of Figure 2. The trace element concentrations in the "organic" and "inorganic" components of the original kerogen, as determined by this method, are listed in Table 2.

3. Determination of Organic and Inorganic Associations by Analysis of the Mineral Residue.

Pyrite and marcasite were the only minerals identifiable by XRD in the mineral residue. After removal of pyrite and marcasite with HNO_3, however, the XRD pattern confirmed the presence of chalcopyrite, rutile and anatase as minor mineral components in the kerogen. The trace element concentrations in the mineral residue before and after the HNO_3 treatment are shown in Table 3 and confirm the XRD data. A number of elements (e.g., As, Co, Fe, Mn, Mo, Ni, S, and Sb) are 90-100% leached by $3MHNO_3$. These elements are thus associated with pyrite, marcasite or other minerals which are soluble in dilute HNO_3 (but not in HCl/HF). As a result, the inorganic associations for these elements in the kerogen may be accounted for based upon their dissolution in the HNO_3 relative to the dissolution of Fe. The assumptions made in this method for estimating mineral associations are as follows:

1) The mineral residue is representative of the inorganic component of the original kerogen. This will not be true for neoformed fluorides (e.g., ralstonite).

2) The fraction of Fe in organic form in the kerogen is small.

3) The amount of an element dissolved is proportional to the amount of Fe dissolved. This will not be the case for elements associated with ralstonite (Na, Mg, Al, etc.).

This technique is limited to elements which form sulfides but may be more reliable for most of these elements than the density fractions method as a result of the basic assumptions behind each method. A correction for Se, however, cannot be made due to the formation of elemental S (and hence elemental Se) during the pyrite dissolution. The data for Cu in Table 3 indicate that roughly 4% of the sulfur in the HNO_3-treated mineral residue sample is in the form of chalcopyrite leaving ~20% of the sample as elemental S. Thus, the true inorganic Se content would be underestimated in this "pyrite dissolution method" because of the chemical similarities between S and Se, i.e., oxidation of H_2Se to Se^o by HNO_3 would occur. The inorganic contributions to the original kerogen trace element content, as determined by this method, are listed for several elements in Table 4 (see also Table 2).

4. EMP-XRF Analysis. Electron micrographs and elemental distributions of the ashed kerogen indicate that both framboidal and massive type pyrite/marcasite are present in the kerogen. Analysis of mineral grains shows that Ni is present in both forms of pyrite/marcasite and in the chalcopyrite but not in rutile. The Ni X-ray data also indicates that Ni is present at higher concentrations in the framboidal pyrite than in the massive pyrite. Semiquantitative EMP-XRF data gave Ni concentrations of approximately 0.04 ± 0.02 percent and 0.01 ± 0.01 percent for framboidal and massive type pyrites, respectively. Correction for the Ni content of the kerogen in pyritic form thus cannot be made from the analysis of individual massive pyrite grains.

4. Determination of Inorganic/Organic Associations by the LTA Method.

Previously in this laboratory, the inorganic associations of the elements in kerogens were based upon the LTA of the kerogen (11). In this method the organic matter was oxidized using LTA and the ash was treated with dilute HCl to remove oxides formed in the ashing process. The remaining mineral matter was then considered to be representative of the inorganic fraction of kerogen. In this study a similar procedure was followed for both float and sink kerogen fractions. The ash and HCl-treated ash samples were analyzed by XRD and INAA. The results of these analyses are shown in Table 5. The XRD patterns of both the float and sink ashes revealed the presence of the neoformed fluoride ralstonite. The XRD patterns of the HCl-treated ashes and the trace element data in Table 5 indicate that the ralstonite is soluble in dilute HCl after ashing. Hence, as suggested by Van Berkel and Filby (11) the LTA method cannot be used to determine the organic association of fluorides that precipitate as ralstonite (Na, Mg, Al, etc.) or which coprecipitate with ralstonite.

A major problem with the LTA technique is the partial oxidation of sulfide minerals (pyrite or marcasite) during the ashing procedure. The float ash consistently had a rust color on its surface after a few hours in the asher. This color is a result of the oxidation of pyrite (to Fe_2O_3) as confirmed by the deep yellow color of the HCl wash of the ash and the analytical data in Table 5. Thus, the Fe and other metals leached from oxidized sulfide minerals are not the result of oxidized organic complexes. Because pyrite contains Ni and other transition metal complexes, correction for the contribution of each element in the oxidized pyrite would have to be made. Because the forms of pyrite may have different composition, the correction cannot be based on the composition of the residual pyrite.

CONCLUSIONS

New Albany kerogen concentrates isolated by the scheme shown in Figure 1 were found to contain several residual minerals identified by XRD. Several elements (As, Co, Mo, Mn, Ni, Sb, Se, Zn) appeared to have some association with the major residual mineral, FeS_2, or with other less abundant inorganic forms which were soluble in 3M HNO_3. Of these elements only Mn was found to have no significant contribution to the organic fraction of the kerogen. The remaining elements, along with V, were shown to have substantial organic associations and may be useful in future work on oil-source rock correlations using trace elements.

The results of the two techniques used to quantify the inorganic fraction of the kerogen are compared in Table 6 for the elements mentioned above. The data for the organic compound shows good agreement between the two techniques. For the mineral component agreement for most elements between the two methods is good, except for Mo, Sb, and Se.

It is evident that although the methods allow calculation of organic/inorganic associations of elements in the kerogen isolated from the shale, the "true" concentrations of these elements in the kerogen in the shale cannot be determined. Undoubtably the isolation procedure removes labile elements from the kerogen and adds artifact minerals (ralstonite).

REFERENCES

1. Abu-Elgheit, M., Khalil, S.O., and Barakat, A.O., Prepr. Div. Petrol. Chem. ACS 24, 793-97 (1979).

2. Ellrich, J., Hirner, A., and Stark, H., Chemical Geology 48, 313-23 (1985).

3. Hitchon, B. and Filby, R.H., Bull. Am. Assoc. Petrol. Geol. 68, 838-49 (1984).

4. Curiale, J.A., in "Metal Complexes in Fossil Fuels," R.H. Filby, and J.F. Branthaver, Editors, ACS Symposium Series No. 344, American Chemical Society, Washington, DC, 1987.

5. Van Berkel, G.J., Ph.D. Thesis, Department of Chemistry, Washington State University (1987).

6. Odermatt, J.R., Curiale, J.A., Hirner, H.V., Mercer, G.E. and Filby, R.H., "Determination of Metals in Kerogens: A Comparative Study". Abstract, 197th ACS meeting, Dallas, TX, April 1989.

7. Durand, B. and Nicaise, G., in "Kerogen: Insoluble Organic Matter from Sedimentary Rocks," B. Durand, Editor, Editions Technip, Paris, 1980.

8. Saxby, J.D., in "Oil Shale," T.F. Yen and G.V. Chilingarian, Editors, Elsevier, Amsterdam, 1976.

9. Robinson, W.E., in "Organic Geochemistry", G. Englinton and M.T.J. Murphy, Editors, Springer Verlag, Berlin, 1969.

10. Hasenmueller, N.R., Woodward, G.S. "Studies of the New Albany Shale (Devonian and Mississippian) and equivalent strata in Indiana"; Indiana Geological Survey Contract Report to U.S. Department of Energy, Contract DE-AC-21-76MC05204, 1981; 100 p.

11. Van Berkel, G.J. and Filby, R.H. in "Geochemical Biomarkers", T.F. Yen and J.M. Moldowan, Editors. Horwood Academic Publishers, London, 1988.

12. Van Berkel, G.J., Filby, R.H. and Quirke, J.M.E., Org. Geochem. 14, 119 (1989).

13. Jacobs, F.S., and Filby, R.H. Anal. Chem. 55, 74-7 (1982).

Table 1. Trace element data for New Albany kerogen and density fractions.

Element (µg/g)	Original Kerogen	Float Fraction (d<1.48)	Sink Fraction (d>1.48)	Mineral Residue
Al	4120	3920	11400	2400
As	114	62.7	308	810
Co	130	120	166	187
Cr	41.2	40.1	86	192
Cs	8.16	7.35	21.4	0.838
Fe	48800	17200	177000	376000
Hf	3.09	0.566	10.4	61.0
La	32.6	25.5	79.0	78.8
Mg	2690	<3000	4020	<1500
Mn	47.0	11.5	173	417
Mo	2190	2380	2190	1290
Na	1900	1600	4940	500
Ni	2000	2090	1430	947
Rb	129	135	369	<40
Sb	62.3	70.8	53.7	60.2
Sc	2.90	2.35	7.58	4.56
Se	181	178	202	186
Sm	3.37	3.04	7.01	12.0
Ta	1.93	1.97	2.45	3.33
Ti	2270	730	9540	19000
V	980	1070	541	140
Zn	82.8	78.0	135	258
Zr	154	84.2	442	1960
Mass Used/ Recovered	10.0g	7.9g	1.5g	0.086g

Table 2. Trace element concentrations in mineral and organic components of kerogen calculated from density fractions.

Element (Mg/g)	Concentration in kerogen	Concentration in organic fraction	Concentration in mineral fraction
Al	4120	3117	8991
As	114	36.4	557
Co	130	115	213
Cr	41.2	35.2	133
Cs	8.16	5.84	35.7
Fe	48800	0	340000
Hf	3.09	0	20.4
La	32.6	19.8	133
Mg	2690	--	--
Mn	47.0	0	337
Mo	2190	2400	1997
Na	900	1240	8330
Ni	2000	2160	760
Rb	129	110	606
Sb	62.3	72.6	36.3
Se	2.90	1.79	7.88
Sc	181	175	226
Sm	3.37	2.61	11.0
Ta	1.93	1.92	2.94
Ti	2270	0	18500
V	980	1130	0
Zn	82.8	71.9	193
Zr	154	45.8	805

Float f_{10} = 0.9494 f_{1m} = 0.0506
Sink f_{20} = 0.4782 f_{2m} = 0.5218

Table 3. Trace element concentrations in mineral residue sample before and after 3M HNO_3 treatment.

Element (µg/g	Mineral Residue (100%)	HNO_3-Treated Mineral Residue (16%)	Percent Mass Lost
Al	2240	8150	41.8
As	626	38.1	99.0
Co	224	27.1	98.1
Cr	137	829	3.2
Cu	4800	31600	0.0
Cs	1.20	<0.58	--
Fe	390000	32100	98.7
Hf	31.1	182	6.4
La	97.7	12.3	98.0
Mg	1140	1460	79.5
Mn	408	32.1	98.7
Mo	1250	520	93.3
Na	448	814	70.9
Ni	905	1510	73.3
Rb	29.0	<17	--
S	452000	240000	91.5
Sb	40.8	28.3	88.9
Sc	3.37	18.7	11.2
Se	247	649	58.0
Sm	13.8	11.7	86.4
Ta	2.62	16.6	0.0
Ti	8760	66800	0.0
V	98.4	580	5.7
Zn	330	726	64.8
Zr	997	5610	10.0

Table 4. Trace element contents of organic and mineral components for elements showing solubility in dilute HNO_3.

Element (µg/g)	Original Kerogen	Percent Organic	Concentration in Organic Fraction*	Concentration in Inorganic Fraction
As	114	31.1	41.2	540
Co	130	78.5	119	192
Fe	48800	0	0	336000
La	32.6	62.8	23.9	82.5
Mn	47.0	0	0	323
Mo	2190	93.2	2390	1010
Ni	2000	95.8	2240	578
Sb	62.3	71.3	52.0	123
Se	181	90.0	191	124
Zn	82.8	67.2	65.1	187

*Using f_{10} = 0.8546 for kerogen.

Table 5. Trace element data for low temperature ash and HCl-leached ash from kerogen density fractions.

Element (µg/g)	Kerogen* Float 100%	Float Ash 14%	Float Ash-HCl 4.2%	Kerogen Sink 100%	Sink Ash 55%	Sink Ash-HCl 33%
Al	8530	54200	4540	30300	49900	7630
As	64.6	444	340	265	492	564
Co	138	947	590	195	358	228
Cr	31.3	227	240	69.8	125	152
Cs	12.3	88.7	5.87	42.3	74.0	9.19
Fe (%)	1.46	10.5	21.7	13.1	26.2	40.1
Hf	0.299	2.29	7.13	6.53	13.7	19.9
La	36.2	254	33.5	158	274	60.8
Mg	4100	26500	1380	12300	22500	1390
Mn	9.11	61.6	172	166	270	418
Mo	2390	16700	1590	2080	3810	216
Na	2880	20500	1100	10300	18000	2060
Ni	2260	16200	2020	1710	3080	810
Rb	194	1520	197	733	1250	309
Sb	77.7	536	26.9	57.8	102	24.1
Sc	3.69	27.0	2.82	12.6	21.7	5.34
Se	145	576	201	270	396	178
Sm	3.01	22.3	3.85	11.4	20.7	8.46
Ti	<960	<2300	3940	4060	7530	9820
V	911	6480	358	491	950	66.8
Zn	86.1	587	207	145	293	292
Zr	102	602	268	291	542	481

*Percentages refer to mass of original unashed and untreated sample. HCl refers to ash leached with 2M HCl.

Table 6. Comparison of trace element concentrations calculated by the pyrite dissolution method (PDM) to the density fraction method (DFM).

Element (µg/g)	Organic Fraction PDM	Organic Fraction DFM	Inorganic Fraction PDM	Inorganic Fraction DFM
As	41.2	36.4	540	557
Co	119	115	192	213
Fe	0	0	336000	340000
La	23.9	19.8	83.9	133
Mn	0	0	323	337
Mo	2390	2400	1010	2000
Ni	2240	2160	578	760
Sb	52.0	72.6	123	36.3
Se	191	175	124	226
V	1150	1130	0	0
Zn	65.1	11.9	187	193

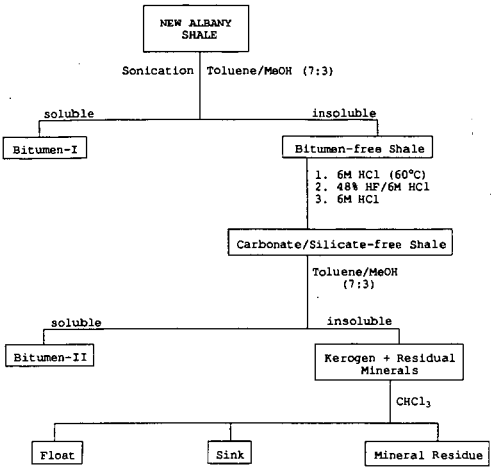
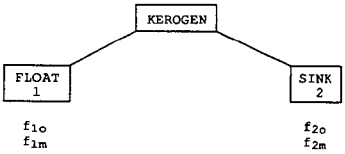


Figure 1: Kerogen Isolation Scheme



f_{1o} f_{1m} $\qquad$ f_{2o} f_{2m}

$f_{1o} + f_{1m} = 1 \qquad f_{2o} + f_{2m} = 1$

Vanadium concentration organic = V_o
Vanadium concentration mineral = V_m

$$V1 = (f_{1o})(V_o) + (f_{1m})(V_m) \qquad V_2 = (f_{2o})(V_o) + (f_{2m})(V_m)$$

Assume $V_m << V_o$, Hence

$$\frac{V_1}{V_2} = \frac{f_{1o}}{f_{2o}}$$

For iron, assume $Fe_m >> Fe_o$

$$\frac{Fe_1}{Fe_2} = \frac{f_{1m}}{f_{2m}}$$

Thus, for each element X

$$X_1 = (f_{1o})(X_o) + (f_{1m})(X_m)$$
$$X_2 = (f_{2o})(X_o) + (f_{2m})(X_m)$$

f_{1o}, f_{2o} = weight fraction organic in float and sink

f_{1m}, f_{2m} = weight fraction inorganic in float and sink

Figure 2: Calculation of organic/inorganic associations from density fractions