NRC Publications Archive
Archives des publications du CNRC

Characterization of humic matter associated with heavy minerals from oil sand
Majid, Abdul; Ripmeester, John A.

National Research Council Canada   Conseil national de recherches Canada

Canada

Chapter 19

Characterization of Humic Matter Associated with Heavy Minerals from Oil Sand

Abdul Majid and John A. Ripmeester

Division of Chemistry, National Research Council of Canada, Ottawa, Ontario K1A 0R9, Canada

Humic matter associated with heavy metal minerals present in Athabasca oil sands, was isolated using sodium hydroxide extraction and by dissolving the mineral matter in acids. These fractions were analysed by elemental analysis and infrared, proton and ^{13}C NMR spectroscopy. Comparison of this data with the corresponding data for humic acids from sub-bituminous coal and peat and asphaltenes from bituminous feed stock, suggest the similarity of this humic material with humic matter from sub-bituminous coal. It appears to have very little potential for hydrocarbons production because of its position in the Van Krevelen diagram. Origin of this organic matter could be different from that of the greater part of the bitumen of the Athabasca oil sands.

Athabasca oil sand is a complex, variable mixture of bitumen, sand, water and clays (1). The total reserves of oil sand deposits are estimated to contain close to 2.15×10^{11} m^3 of bitumen in place (2-5). The Athabasca deposit is currently under commercial exploitation, by Suncor and Syncrude using the hot water extraction process developed in the 1920's by K.A. Clark (6). This process results in very large volumes of tailings, consisting mainly of sand and a dispersion of various clays containing residual organic matter (1,7-9). The sand settles rapidly from the tailings and is used to build containment dikes for aqueous sludges that show little tendency to dewater, even when subjected to mechanical dewatering procedures (10). It is the buildup of these partially settled clay sludges which presents not only an environmental problem but also a significant repository for non-recycleable water.

The reason for the intractability of the clay slimes has been a subject of considerable study (1,7,9,11-13). Considerable quantities of insoluble organic material are known to be associated with these clay slimes (8,14-15). Most of this organic material is strongly associated with the mineral fines and is insoluble in organic solvents under mild conditions (16).

Based on the results of published work it is generally
believed that the interaction of organics with the clay minerals is
important in determining the nature of the oil sand slimes
(8,14-15). The interaction is thought to provide a hydrophobic
character to the clay particle surfaces allowing bridging through
residual bitumen to set up a weak gel structure.

Relatively little information is currently available concer-
ning the nature of the unextractable organic matter. In a recent
publication Ignasiak et al. have reported that this organic matter
consists of humic and non-humic components containing numerous
oxygen functions (17). In our previous work we have attempted to
isolate and then concentrate this organic matter using oil phase
agglomeration and acid dissolution techniques followed by the
removal of soluble organic material by a Soxhlet extraction method
using benzene/methanol (8,18-19). These organic materials were
then studied using elemental analyses and spectroscopic techniques.
The data was discussed in terms of the chemical structure and the
nature of bonding between the mineral phase and the organic phase
of oil sands.

In this investigation we have attempted to isolate this
strongly bound organic matter from heavy metal mineral fractions by
successive extractions with aqueous sodium hydroxide over a
prolonged period of time. Elemental analyses and spectroscopic
techniques were used for the characterization of organic material
from oil phase solids (OPS). Comparisons have been made among peat
and coal humic acids, asphaltenes from oil sand bitumen and the
organic matter adhering to the mineral fines in oil sands in an
attempt to understand the formation of oil sand deposits. It is
also hoped that study might provide insight into beneficiation and
enrichment of the organic matter in low grade oil sands that are
known to contain significant quantities of unextractable organic
matter (16).

Experimental Methods

Sample Description. Aqueous tailings in 5-gallon to barrel-size
lots were obtained from the Suncor plant sludge pond, and contained
5-12% solids by weight, although in some lots the solids content
ranged as high as 30%.

Oil Phase Solids. Oil phase solids (OPS), the heavy metal minerals
fraction containing unextractable organic matter were isolated from
Suncor sludge using oil phase agglomeration techniques reported
elsewhere (19).

Humic Acid Extraction. Figure 1 is a flow-sheet for the extraction
of humic and fulvic acids from oil phase solids (OPS). A 20g
sample of oil phase solids (OPS) was digested with 200 ml 2%
aqueous NaOH at 70°C under N_2 for a period of one month. The
digestion was repeated six times with successive fresh portions of
aqueous NaOH solution, decanting the spent NaOH each time. The
alkaline solution was subsequently separated from the sand by
centrifugation, and acidified to pH 2 with 5N HCl. After 24 hours,

OIL PHASE SOLIDS (OPS)

aqueous 2% NaOH digestion

| RESIDUE | | SOLUBLES |

aqueous HCl

| SOLUBLES | | PPT, HUMIC ACIDS |

dialized against distilled H_2O

| Cl free Solution | evaporated to dryness

methanol extraction

| SOLUBLES | | RESIDUE |

acetone extraction

| SOLUBLES | | RESIDUE |

solvent evaporation

| RESIDUE |

methanol extraction

| SOLUBLES | | RESIDUE |

solvent evaporation

| FULVIC ACIDS | dried under vacuum at 60°C

Figure 1   Flow sheet for the extraction of Humic and Fulvic Acids.

the precipitated humic acids were recovered from the solution by
filtration.   The precipitate was washed several times with 1% HCl.
The total amount of humic acids extracted after six extractions
corresponded to 12.0% of the weight of the OPS.   Although more
humic acids could be extracted from OPS, complete recovery of humic
matter from OPS was an extremely time consuming procedure and hence
stopped after six extractions.

Fulvic Acid Extraction. The solution obtained after removal of humic acids was dialized against distilled water until free of Cl, and then concentrated by evaporation of water at 50°C. The residue was then extracted with methanol, followed by acetone. The two extracts were combined, the solvents distilled, and the residue was repeatedly redissolved in methanol until no residue was observed. Finally, the solvent was removed from the clear methanol solution, yielding the fulvic acids. The humic and fulvic acids were dried in a vacuum oven at 60°C to constant weight.

Bitumen. Analytical data reported for bitumen from bituminous feed stock sand was taken from a round robin study (20). The sample used in this study was a coker feed bitumen from Suncor, obtained in February, 1981.

Asphaltenes. Asphaltenes were precipitated from benzene solution of the above mentioned bitumen by the addition of a fifty fold excess of n-pentane over a period of 4-6 hours while stirring under N_2. the precipitated asphaltenes were filtered through a Whatman filter paper #42, washed several times with n-pentane until the filtrate became almost colorless and finally dried in a vacuum oven at 60°C.

Humic Acid from Oil Sand. Analytical data reported for humic acid extracted from oil sands was taken from D.S. Montgomery (21).

Organic Matter from Low Grade Oil Sands. A low grade oil sand sample (bitumen content ≈5%) obtained from Alberta Research Council sample bank was used for isolating the toluene insoluble organic matter associated with the mineral fraction of oil sands. The sample was first extracted with toluene in a Soxhlet apparatus for 48 hours. Residue was dried at 100°C overnight and then treated with 6 N HCl to decompose carbonates, followed by digestion with concentrated HCl to dryness. The residue was repeatedly washed with warm water until free from chloride. It was then digested with 35% HF to dryness and washed repeatedly with warm water until the washings became neutral. The organic matter concentrate so obtained was then dried under vacuum at 50°C.

Elemental Analysis. C, H and N analyses were performed using a Perkin-Elmer model 240 CHN analyser. Mineral carbon was measured titrimetrically after acid digestion. Organic carbon was then determined by subtracting carbonate carbon from total carbon. Sulfur was analysed as total sulfur using X-ray fluorescence spectroscopy. Oxygen was determined directly (20). For mineral samples containing adsorbed organic matter, the ultimate analysis was done at the Energy, Mines and Resources laboratory using ASTM procedure D271.

Ash Content. Ash content of oil phase solids and their solid fractions was determined by heating at 380 ± 10°C to constant weight. After cooling to room temperature, the samples were soaked in water for 4 hours and finally dried at 110°C to constant weight. The difference between the initial and the final weights was taken as "loss-on-ignition" (21).

<u>Instrumental Analysis</u>. Infrared spectra were recorded using a Perkin-Elmer model 683 IR spectrometer. Samples were run as KBr pellets.

Proton NMR measurements were performed on a Bruker MSL 300 NMR spectrometer (300 MHz). The spectra were recorded in solution in NaOD and deuterated DMSO.

All solid state C-13 NMR spectra were obtained at 22.6 MHz on a Bruker CXP180/90 NMR spectrometer using the cross polarization (CP) technique with magic angle spinning (MAS). A contact time of 1 ms and a repetition time of 2s were selected. The magic angle spinning speeds were 3.0-3.4 KHz. Chemical shifts were determined by position relative to tetramethylsilane (TMS). Each spectrum was the Fourier transform of 3000-10000 free-induction decay curves.

C-13 solution spectra of ≈5% humic acid in NaOD were run at 75.47 MHz on Bruker MSL 300 NMR spectrometer, employing inverse gated decoupling and 30,000-40,000 45° pulses at intervals of 3 seconds.

Results and Discussion

A typical analysis of the heavy metal mineral fraction containing unextractable organic matter (oil phase solids, OPS, loss on ignition at 380°C, 32.5%) is given in Table I.

Table I
Analytical Data for a Typical Oil Phase Solid Sample

	wt.%
Carbon	19.3
Hydrogen	1.4
Nitrogen	0.3
Sulfur	3.5
SiO_2	13.0
Al_2O_3	5.0
Ti	18.0
Zr	2.0
Fe	8.6
Cu	0.05
Ni	0.03
Mn	0.21
Zn	0.04

The fact that a major portion of this organic matter associated with heavy metal minerals can be extracted with aqueous NaOH, strongly suggests the humic nature of this organic matter. One of the most important characteristic of humic substances is their ability to interact with metal ions, metal oxides and metal hydroxides to form associations of widely differing chemical and biological stabilities (22, 23). It is believed that ion exchange, surface adsorption, chelation, coagulation and peptization processes are involved in such interactions (24-26). Also, the

humic substances are known to form both chelated and ionic complexes with Al, Ba, Co, Cr, Cu, Fe, Mn, Ni, Ti and V(27-30). It is therefore, very likely that most of the metals occuring in OPS are associated with the humic matter in the form of humic matter-metal or metal oxide complexes.

The elemental compositions of bitumen, asphaltenes, organic matter from a sample of toluene extracted low grade oil sand, humic acid extracted from oil sands, OPS and humic and fulvic acids extracted from OPS are given in Table II. Examination of the data leads to the following conclusions:

Table II
Elemental Analyses (in Percentage of dry, ash free basis)

Sample	wt. %					Atomic Ratios	
	C	H	N	S	O	H:C	O:C
Humic Acid extracted from OPS	67.37	4.40	1.00	3.0	24.23	0.78	0.237
Fulvic Acid extracted from OPS	39.23	5.05	1.12	10.24	44.36	1.54	0.848
Organic Matter associated with OPS	61.24	5.22	2.82	4.15	26.57	1.02	0.33
A Typical Oil Sand Bitumen Sample	83.01	10.48	0.44	4.74	0.91	1.51	0.008
Asphaltenes from Oil Sand Bitumen	80.87	8.32	1.02	7.61	2.29	1.23	0.021
Humic Acid from Oil Sands	67.41	4.34	1.42	2.66	24.17	0.77	0.27
Organic Matter from Low Grade Oil Sands	57.0	4.8	–	15.5	22.67	1.01	0.30

1. The elemental composition of the humic acid extracted from OPS is remarkably similar to that of the one extracted from oil sands. Both of these substances have considerably higher carbon content and lower nitrogen and oxygen contents compared with the soil or aquatic humic acids (28). The composition of the humic acids extracted from OPS and oil sands resembles that of coal humic acid more so than aquatic or peat humic acids (28).

2. Oxygen is the most abundant heteroatom in OPS, humic and fulvic acids, and toluene extracted low grade oil sands organic matter.

3. The carbon content of these fractions is considerably lower compared to those of the corresponding asphaltene and bitumen of the bituminous sand feedstock.

4. The sulfur content of the fulvic acid and toluene extracted oil sands is considerably higher than those of other fractions presumably due to the presence of inorganic sulfur (19).

5. The nitrogen content of OPS is about twice that of humic and fulvic acids extracted from it.

Comparable elemental compositions of the humic acids extracted from oil sands and OPS suggest that no appreciable alteration of the humic matter occurs either during hot water extraction of bitumen from oil sands or during storage in the tailings ponds.

Higher oxygen content of these fractions is typical of humic materials as these materials are known to contain considerable quantities of oxygen containing functional groups such as carboxyls, phenolics, alcholic hydroxyls, carbonyls and methoxyls (28).

Lower nitrogen content of humic and fulvic acid fractions compared with the feed stock could be due to the loss of some nitrogen by hydrolysis of some nitrogen compounds during extraction (31). Also one of the reviewers has suggested that NaOH may have left N-containing material unextracted on the OPS.

The Van Krevelen diagram, which is a graph of atomic H/C versus O/C ratios provides a useful approach for the characterization of coals, kerogens and humic matter (32-33). These materials can be classified into one of the three types based on the Van Krevelen diagram.

Humic and unextractable organic matter from oil sands were plotted on the Van Krevelen diagram as shown in Figure 2. All of these fractions appear to be similar to type 3 kerogens. These types of kerogens are known to be comprised of an important proportion of polyaromatic nuclei and heteroatomic ketone and carboxylic acid groups (33). Aliphatic groups are subordinate constituents in varying proportions of this organic matter. They consist of a few long chains originating from higher plant waxes, some chains of medium length from vegetable fats, methyl groups and other short chains. This type of organic matter is derived essentially from terrestrial plants, and is incorporated in sediment either directly or through its alteration products in the form of soil humic acids. Humic coals have been classified under this category (34). This type of organic matter is least favourable for oil generation (33).

Infrared Spectra. The infrared spectra provide some indication of the chemical nature of the material. It enables one to detect the presence of chemical groups, preclude or limit the existence of proposed structures, and demonstrate similarities and differences in chemical structure of the organic materials studied. Infrared

spectra of humic acid, fulvic acid, OPS and a sample of asphaltenes are shown in Figure 3. The assignment of the various bands is based on the published work for coal, asphaltenes and humic materials (35-45). The main zones of interest are as follows:

1. A broad absorption band around 3200-3400 cm^{-1}, related to H-bonded OH groups (phenolic, alcoholic, carboxylic OH), small contributions from N-H groups being also possible;

2. Weak to strong absorptions in the ≈2900 cm^{-1} region are attributed to CH_2 and CH_3 aliphatic groups;

3. A broad band centered at 1720 cm^{-1}, related to various C=O groups (ketones, acids, esters);

4. A medium intensity broad band centered at 1600 cm^{-1}, attributed partly to conjugated C=C bonds and partly to carbonyl of ketones and/or quinones;

5. Varying intensity bands at 1450 and 1380 cm^{-1} are due to bending frequencies of asymmetric $C-CH_3$ bond and/or methylene and symmetric $C-CH_3$ bond respectively.

6. A group of bands located around 1100, 1030 and 900 cm^{-1} are assigned to C-O stretch in aromatic oxygenated compounds, such as aromatic ethers, sulfoxides and polysaccharides.

7. Strong bands in the infrared spectrum of fulvic acid at 800, 650 and 550 cm^{-1} are considered aromatic out of the plane frequencies and are important with regard to the nature of the structure of aromatic clusters.

Fulvic acid shows a strong absorption at 3200 cm^{-1} compared with humic acid and OPS. This indicates much higher OH groups contents in fulvic acid compared with other fractions suggesting greater hydrogen bonding.

Humic acid has a stronger absorption in the 2900 cm^{-1} region compared with weak absorption for fulvic acid. This indicates the presence of greater numbers of CH_2 and CH_3 groups in humic acid compared with the fulvic acid. Two bands at 2420 and 2340 cm^{-1} in the infrared spectrum of fulvic acids appear to be due to the presence of an impurity. Phosphates are known to absorb in this region (46). Fulvic acid has an extremely large and broad absorption at 1450 cm^{-1} compared with well resolved weak absorptions at 1450 and 1380 cm^{-1} for humic acid, asphaltenes and OPS. The much higher intensity of this band compared with the CH stretching vibrations around 2900 cm^{-1} preclude the assignment for this band due to deformation vibrations of CH_3 and CH_2 groups. Ignasiak et al. have recently reported a similar pattern in a polar fraction extracted from oil sands (17). They assigned this absorption to strongly polarizable carbonyl groups such as diketones and/or α, β-unsaturated ketones complexed to $FeCl_3$. The presence of considerable quantities of iron in the ash from fulvic
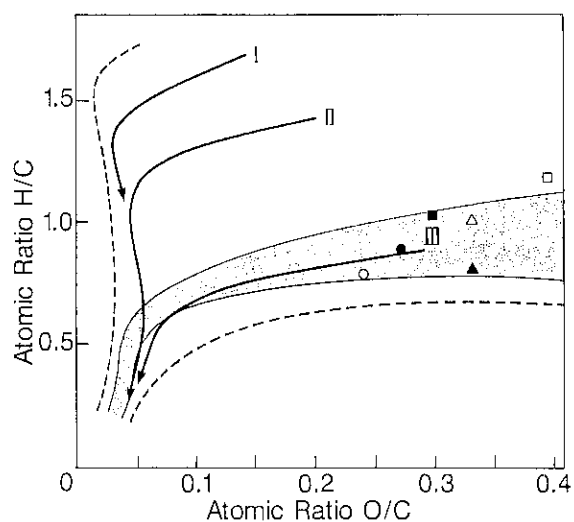
Figure 2. Van Krevelen diagram showing the principal types and
           evolution paths of kerogens. OPS, Δ; Humic acid
           from OPS, O; Peat,☐; Coal humic acid, ▲; Lignites,
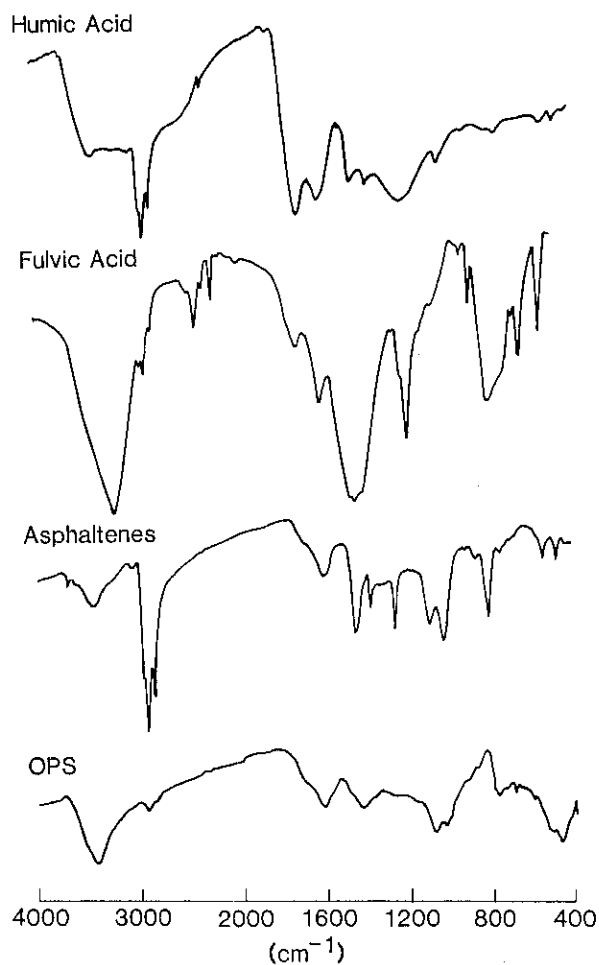   ●; Organic matter from low grade oil sand,■.

Figure 3. Infrared spectra of OPS, humic and fulvic acids and
           asphaltenes.

acid supports the possibility of such an assignment in the present case.

The absorption due to C-O stretching and OH deformation of COOH group and aryl ethers, is stronger and sharper for fulvic acid compared with humic acid.

Bands for the aromatic out of plane frequencies around 800-500 cm^{-1} are also much stronger for fulvic acid compared with humic acid.

The essential features of the humic and fulvic acid spectra are the same as of OPS and asphaltenes. The major difference in the spectrum of fulvic acid from those of other fractions is the relative intensities of the various bands.

Proton NMR Spectra. Figure 4 shows the proton NMR spectra for humic and fulvic acids. General features of the two spectra are similar. However, the humic acid spectrum shows a relatively sharper and stronger signals compared with the fulvic acid spectrum. Both spectra show a resonance around 0.7 ppm due to $-CH_3$ protons. Humic acid shows two signals due to $-CH_2$ protons at 1.0 and 1.1 ppm. Corresponding signals in the fulvic acid spectrum are located at 1.0 and 1.3 ppm. Weak signals around ≈ 2.0 ppm in the fulvic acid spectrum could be due to the hydrogen on carbon atoms α to ring.

Aromatic protons appear as a broad signal between 7-9 ppm in the humic acid spectrum. Fulvic acid has a barely detectable broad signal partly overlapped by the residual protons from heavy water.

^{13}C NMR Spectra. The CP/MAS-^{13}C nmr spectra of the strongly bound organic matter associated with heavy metal minerals and fines from oil sands and three humic acid samples extracted from OPS, sub-bituminous coal, and a sample of peat are shown in Figure 5. Interpretation of the ^{13}C nmr spectra has been based on the published data on humic substances and coal related materials (47-57). The spectra are poorly resolved and show only bands rather than sharp peaks.

The presence of a broad range of aliphatic compounds in all the spectra is indicated by the resonance in the 10-50 ppm range. The large peak at 30 ppm is due to the presence of a number of repeating polymethylene units in humic macromolecules. The presence of two small peaks at ≈ 14 and 20 ppm in the spectrum of OPS humic acid sample indicates the presence of long-chain-terminating methyl groups. A small signal at 38 ppm in the spectrum of humic acid from OPS could be due to the bridgehead or other CH naphthenic carbons.

As the nitrogen content is low compared to the oxygen content for these samples, carbohydrates, ether and methoxy groups are expected to be the major contributors to the resonance in the 50-100 ppm region. Distinct bands in this region are displayed by the Peat humic acid and OPS humic acid. It is most likely that
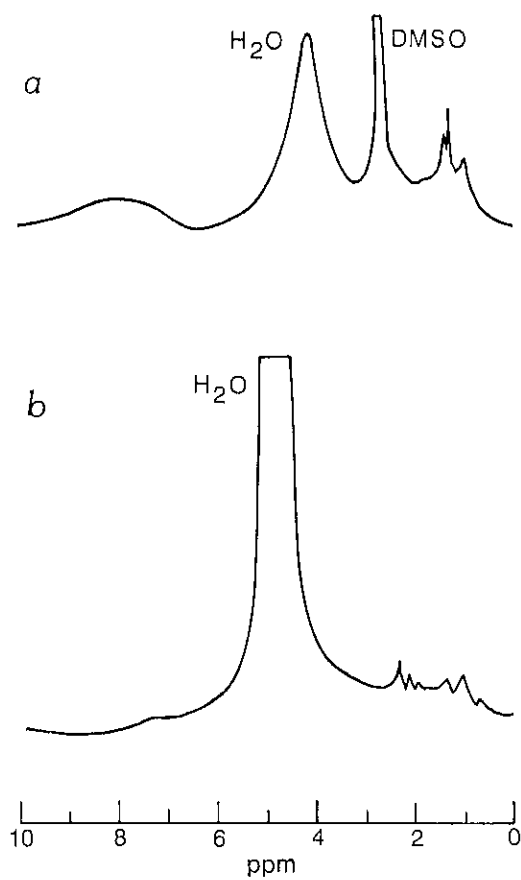
Figure 4.   Proton NMR spectra of a) Humic acid from OPS, b)
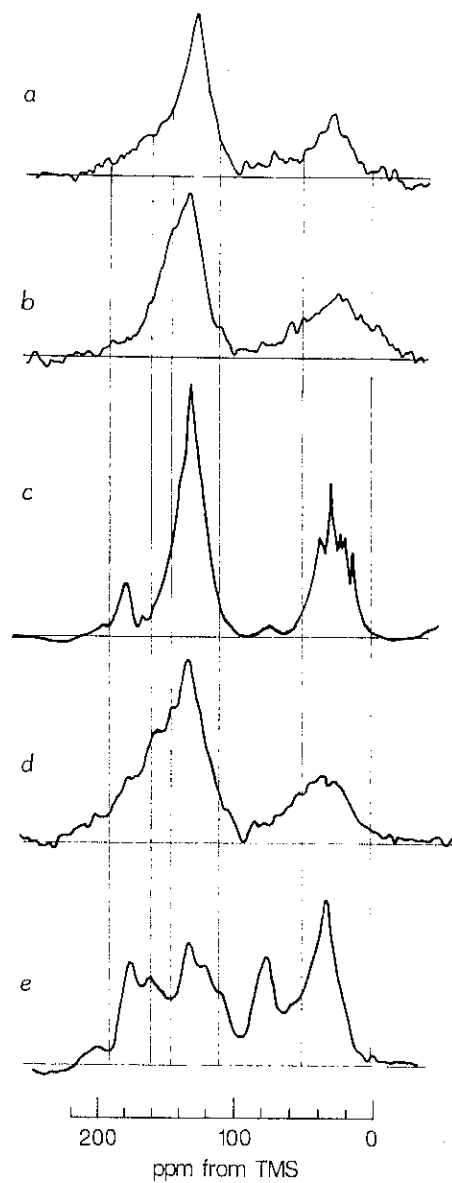   Fulvic acid from OPS.

Figure 5.   CP/MAS ^{13}C NMR spectra of a) Toluene extracted low
grade oil sand, acid leached b) OPS, d) humic acid
from sub-bituminous coal and e) peat humic acid, and
c) ^{13}C NMR spectrum of humic acid from OPS in NaOD.

this band is derived from carbohydrates considering the fact that carbohydrates have been identified as major components of some sedimentary humic acids (58). However, the relative contribution of polysaccharides in humic matter from oil sand and sub-bituminous coal is small compared with the Peat humic acid.

The aromatic region extends from 110-160 ppm. Aromatic ether and phenolic carbons appear between 150-160 ppm, aromatic bridgehead and substituted aromatic carbons between 130 and 150 ppm. The phenolic carbons in the humic matter from oil sands are not resolvable as distinct peaks.

A distinct broad peak is observed at ≈180 ppm in the ^{13}C spectra of humic acids from OPS and Peat. This peak represents carboxyl, amide and ester carbons, all of which have been identified as important functionalities of humic acids (58). Additional resonances are observed downfield of the carboxyl resonance in the region of approximately 200-220 ppm. These resonances are characteristic of aldehyde and ketone carbons. Although no distinct resolved peaks are observed, their presence is obvious in the spectra of all three humic acids as a broad band, with contributions of about 0.5-5% of the total signal.

The integration of each spectrum was carried out by division into regions and subsequent determination of their individual areas. The position of regional boundaries in spectra is a matter of definition, as no representative model compounds for these substances are available. The limits were chosen according to Ibarra et al. and Verheyen et al. (55,56). The spectra were divided into four regions as listed in Table III, below.

Aliphatic ethers and alcohols are usually considered to make only a minor contribution to the structure of humic acids (55).

Table III
Assignment of ^{13}C Chemical Shift Ranges

Region	Chemical Shift Range	Carbon Type
A_1	0-50	Aliphatic
A_2	50-110	Aliphatic C-OH, C-OR, Carbohydrate
B	110-145	Aromatic C-H Aromatic C-C Alkyl substituted aromatic carbon
C	145-160	Aromatic C-OH, C-OR
D_1	160-190	Acid, ester, COOH, COOR
D_2	190-230	Aldehyde, ketone

Aliphatic carbon (C_{al}) is given in the spectrum by region A_1 and A_2 and Aromatic carbon (C_{ar}) by region B and C. The quantitative ^{13}C nmr measurements are given in Table IV.

Table IV

Quantitative ^{13}C NMR of Humic Acids and Related Materials

Sample	Area of Total Spectrum (%)					Atomic O/C	Δ	F_a
	A_1+A_2	B	C	D_1	D_2			
OPS	39.1	38.8	12.4	9.2	0.5	0.31	-0.02	56
Humic acid from OPS	43.1	38.7	5.7	9.0	3.5	0.24	0.0	51
Organic matter from low grade oil sands	32.6	46.2	9.3	9.6	2.3	0.31	+0.01	63
Humic acid from sub-bituminous coal	34.0	35.6	12.0	13.8	4.6	0.44	?	59
Peat humic acid	55.4	21.7	7.7	13.4	1.8	0.36	?	35

The contribution of oxygen bound to aliphatic carbons can be estimated, according to Verheyen et al. (56), by comparing the O/C ratios calculated from elemental analysis and by ^{13}C nmr measurements $(C+2D_1+D_2/100)$. If all the oxygen is present in carbonyl, carboxylic and phenolic structures, the ratios calculated by both methods should be comparable. Table IV shows the difference (Δ) between the O/C ratios calculated by the two methods. The results indicate that aliphatic oxygen functions are not significant compared with the proportion of carbonyl, carboxylic and phenolic groups in the humic matter from oil sands.

Table IV also lists the aromaticities calculated by integrating peak areas assigned to aromatic carbons (100-160 ppm) and normalizing to total area less the area of carboxyl carbons (54). It is evident from the table that at least one half of the total carbons in the humic matter from oil sands and sub-bituminous coal are in aromatic locations. The aromaticities of unextractable organic matter from oil sands and heavy metal minerals present in oil sands (OPS) and of humic acids extracted from OPS are comparable to the corresponding value for humic acid from sub-bituminous coal, and much higher compared with the value for peat humic acids. This suggests that the unextractable organic matter from oil sands could be humic matter comparable in maturity to that of sub-bituminous coal.

Conclusions

Significant portion of the organic matter adhering to the heavy metal minerals from oil sands appears to be humic because of its solubility in NaOH. Also, the elemental analysis, infrared and NMR spectroscopic results indicate a remarkable similarity of this organic matter to the humic acid extracted from oil sands. Infrared and NMR spectroscopic results indicate the presence of such species as hydrogen bonded phenols, alcohols, ethers, polysaccharides, amides, polyaromatics with long parafinic chains, carboxylic acids, quinones and ketones. This is again consistent with the material being humic. Most of the above mentioned functionalities are capable of forming chemical bonds with metals, and metal oxides. Chemical bonding between phenols, ethers, amides,

carboxylic acids, quinones and ketones and metals appears more probable.

Humic matter from oil sands has H/C and O/C distributions comparable to the gross composition of peat, lignite and subbituminous coal. It falls in the region of kerogen (III) on the Van Krevelen diagram. This type of organic matter is usually derived from plants of terrestrial origin and is rich in polyaromatic nuclei and heteroatomic ketone and carboxylic acid groups (33). Type III kerogen is not considered to have potential for hydrocarbon generation and usually matures to give coal (33). It appears to be of comparable maturity to that of humic acids from lignite or sub-bituminous coals and is relatively immature when considered in light of its oil generation potential.

These observations are consistent with two possibilities. One is that the entire oil sand deposit is immature, and that bitumen and the type III Humic material simply represent independent development of distinct source materials. Asphaltenes could then be thought of at least as being related to type I Kerogen (33).

The second possibility is that bitumen was formed elsewhere, perhaps in an older formation, and migrated to its current location. In establishing relationships between the different types of organic matter, the role of degradation and the presence of metallic minerals is still largely unknown.

Acknowledgments

Literature Cited

1. Camp, F.W. "The Tar Sands of Alberta, Canada"; Cameron Engineers Inc.: Denver, 1969.
2. Outtrim, C.P.; Evans, R.G. In "The Oil Sands of Canada - Venezuela"; Redford, D.A.; Winestock, A.G., Ed.; Can. Inst. Min. Metallurgy: Montreal, 1977; vol. 1, p. 36.
3. Mossop, G.D. In "Facts and Principles of World Petroleum Occurrance"; Miall, A.D., Ed.: Can. Soc. Petrol. Geol. Memoir: 1980; vol. 6, p. 609.
4. Mossop, G.D. Science 1980, 207, 145-152.
5. Towson, D.E. J. Can. Pet. Technol. 1979, 18, 10-12.
6. Clark, K.A.; Pasternack, D.S. Ind. Eng. Chem. 1932, 24, 1410-1416.
7. Kessick, M.A. Proc. Surf. Phenom. Enhanced Oil Recovery, 1981, p. 559.
8. Ripmeester, J.A.; Sirianni, A.F. J. Can. Pet. Technol. 1981, p. 131.
9. Young, R.N.; Sethi, A.J. J. Can. Pet. Technol. 1978, 76, 76.

10. Camp, F.W. Can. J. Chem. Engin. 1977, 55, 581.
11. Kessick, M.A. CIM Bulletin 1978, 71, 80.
12. Kessick, M.A. International J. Min. Process 1980, 6, 277.
13. Hall, H.S.; Tollefson, E.L. Can. J. Chem. Engin. 1982, 60, 812.
14. Majid, A.; Ripmeester, J.A. J. Separ. Proc. Technol. 1983, 4, 20-22.
15. Kessick, M.A. J. Can. Pet. Technol. 1979, 77, 49.
16. Majid, A.; Sirianni, A.F.; Ripmeester, J.A. Fuel 1982, 61, 477.
17. Ignasiak, T.M.; Zhang, Q.; Kratochvil, B.; Maitra, C.; Montgomery, D.S.; Strausz, O.P. AOSTRA J. Res. 1985, 2, 21.
18. Majid, A.; Ripmeester, J.A.; Davidson, D.W. "Organic Matter Adsorbed to Heavy Metal Minerals in Oil Sands"; NRC, Chem. Div. Rep. #C1095-82S, 1982.
19. Majid, A.; Ripmeester, J.A. Fuel 1986 (in press).
20. Culmo, R. Mikrochimica Acta 1968, 811.
21. Majid, A.; Sparks, B.D. Fuel 1983, 62, 772.
22. Ruggiero, P.; Sciacovelli, O.; Testini, C.; Interesse, F.S. Geochimica et. Cosmochimica Acta 1978, 42, 411.
23. Senesi, N.; Griffith, S.M.; Schnitzer, M. and Townsend, M.G. Geochimica et. Comochimica Acta 1977, 41, 969.
24. Alhksandrova, L.N. Soviet Soil Sci 1967, 7, 903.
25. Broadent, F.E. and Ott, J.B. Soil Sci 1957, 83, 419.
26. Kononova, M.M. "Soil Organic Matter", Pergamon Press, New York, 1966.
27. Cheshire, M.V.; Berrow, M.L. Goodman, B.A.; Mundie, C.M. Geochim Cosmochim Acta 1974, 41, 1131.
28. Schnitzer M. and Khan, S.U. "Humic substances in the Environment"; Marcell Dekker, New York, 1972.
29. Adhikari, M.; Chakrabarti, K.K., and Chakrabarti, G. J. Indian Chem. Soc. 1978, 35, 439.
30. Adhikari, M.; Chakrabarti, G. J. Indian Chem. Soc. 1977, 54, 573.
31. Debyser, Y.; Gadel, F. "Geochemimie Organique des Sediments Marines Profonds"; Orgon I, Mer de Norvege; 1977, 247.
32. Krevelen, van, D.W. "Coal"; Elsevier: Amsterdam, 1961.
33. Tissot, B.P.; Welte, W.H. "Petroleum Formation and Occurrance"; Springer-Verlag: Berlin, 1984.
34. Durand, B.; Monin, J.C. In "Insoluble Organic Matter from Sedimentary Rocks", Durand, B. Ed. Editions Technip; Paris, 1980.
35. Friedel, R.A.; Queiser, J.A. Anal. Chem. 1956, 28, 22.
36. Friedel, R.A.; Retcofsky, H.L. In "Spectrometry of Fuels"; Friedel, R.A. Ed.; Plenum: New York, 1970, 46.
37. Taylor, S.R.; Galya, L.G.; Brown, B.J.; Li, L.C. Spectroscopy Letters 1976, 9, 733.
38. Smith, A.L. "Applied Infrared Spectroscopy"; John Wiley and Sons Inc.: New York, 1979.
39. Wiberly, S.E.; Gonzalez, R.D. Appl. Spec. 1961, 15, 174.
40. Bellamy, L.J. "The Infrared Spectra of Complex Organic Molecules"; John Wiley and Sons Inc.: New York, 1966.
41. Moschopedis, S.E.; Speight, J.G. Fuel; 1976, 55, 334.

42. Jennings, P.W.; Pribanic, J.A.S.; Dawson, K.R.; Bricca, C.E. Preprints Div. of Petroleum Chemistry; American Chemical Society: Washington, D.C., 1981, p. 915.

43. Wen, C.S.; Chilingarian; Yen, T.F. "Developments in Petroleum Science"; American Chemical Society: Washington, D.C., 1978, 7, 155.

44. Stevensen, F.J.; Goh, K.M. Geochimica et Cosmochimica Acta 1971, 35, 471.

45. Gerasimowicz, W.V.; Byler, D.M. Soil Science 1985, 139, 270.

46. Szymanski, H.A.; Erickson, R.E. "Infrared Band Handbook"; IFI/Plenum: New York, 1970.

47. Bartle, K.D.; Ladner, W.R.; Snape, C.E.; Martin, T.G.; Williams, D.F. Fuel 1979, 58, 413.

48. Snape, C.E.; Ladner, W.R.; Bartle, K.D. Anal. Chem. 1979, 51, 2189.

49. Suzuki, T.; Itoh, M.; Takegami, Y.; Watanabe, Y. Fuel 1982, 61, 402.

50. Yoshida, T.; Nakata, Y.; Yoshida, R.; Ueda, S.; Kanda, N.; Maekawa, Y. Fuel 1982, 61, 824.

51. Barron, R.F.; Wilson, M.A. Nature 1981, 289, 275.

52. Dereppe, J.M.; Moreaux, C.; Debyser, Y. Org. Geochem. 1980, 2, 117.

53. Hatcher, P.G.; Vanderhart, D.L.; Earl, W. Org. Geochem. 1980, 2, 87.

54. Hatcher, P.G.; Schnitzer, M.; Dennis, L.W.; Maciel, G.E. Soil Sci. Soc. Amer. J. 1981, 45, 1089.

55. Ibarra, J.V.; Juan, R. Fuel 1985, 64, 650.

56. Verheyen, T.V.; Johns, R.B.; Blackburn, D.T. Geochim. Cosmochim Acta 1982, 46, 269.

57. Hatcher, P.G.; Breger, I.A.; Szeverenyi, N.; Maciel, G.E. Org. Geochem. 1982, 4, 9.

58. Christman, R.F.; Gjessing, E.T. "Aquatic and Terrestrial Humic Materials"; Ann Arbor Sci. Pub: Ann Arbor, 1983.