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# Characterization of oil sands solids closely associated with Athabasca bitumen

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By means of density fractionation, solids associated with bitumen derived from a variety of oil sand grades, were separated into fractions having different humic matter content. Elemental compositions (daf) and calculated densities of the different fractions were similar suggesting a similarity in the nature of the humic matter. Density fractionated solids having a low (<8%) and a high (>87%) ash content were treated with NaOH for various periods of time to extract the humic acids. For all humic acids analysed the elemental composition and distribution of carbon types in each region of  $^{13}$ C n.m.r. spectra were similar. It has been shown that aromatic carbon was the predominant type of carbon for all samples. On the basis of the aromaticity data, it has been suggested that oil sand humic matter has a significant terrestrial input.

#### (Keywords: tar sand; bitumen; aromaticity)

It is generally recognized that many problems encountered in the processibility of oil sand are due to the presence of organic matter insoluble in good solvents for bitumen, such as toluene and dichloromethane<sup>1-5</sup>. The greater part of this insoluble organic matter is known<sup>5</sup> to consist of humic matter. In order to gain a deeper insight into the role that humic matter could play in the processibility of the oil sand, it is desirable to examine the chemical nature and the origin of this material. It is known from our previous work<sup>6</sup> that solids enriched with humic matter could be liberated from the bulk of oil sand solids using the cold water agitation test (CWAT). It has been shown that two fractions of organic rich solids may be distinguished in oil sands: 1, solids closely associated with bitumen and 2, solids which can be isolated in the form of an aqueous suspension. Some properties of the solids suspended in the aqueous phase have been discussed earlier<sup>7</sup>.

The object of the present work was to characterize the organic rich solids closely associated with bitumen. A density separation method, commonly used in soil chemistry<sup>8,9</sup>, was applied to these solids to fractionate them into 'free' organic matter and organic components complexed with inorganic minerals. The chemical composition of the humic matter on different BS fractions is described as well as some characteristics of humic acids derived from these fractions, separated according to density.

#### **EXPERIMENTAL**

The work presented here was carried out on oil sands of estuarine origin obtained from the Syncrude quarry, Fort McMurray, Alberta. The oil sands were ground using a Comomil\* and subsequently mixed to prepare

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homogenized samples, and then stored in sealed containers. The compositions of the oil sand samples studied were determined using Soxhlet extractors in conjunction with Dean and Stark separators<sup>10</sup>. The results (*Table 1*) include the bitumen concentration in three typical oil sands representing the high (I-1), medium (II-2) and low (IV) grades. The series of treatments given to each sample of oil sand is shown schematically in *Figure 1*.

#### Cold water agitation test (CWAT)

The procedure is described in detail elsewhere<sup>7</sup> and is briefly summarized as follows: known amounts of 0.1%Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> solution were added to unextracted oil sand feed stocks. The samples were agitated using a high intensity Spex mixer. As a result of the treatment and settling by gravity the following layers (from the top to bottom) were formed: a bitumen layer (B) which was easily skimmed off, an aqueous suspension layer (A) which was separated by decantation, and a residue layer containing the bulk of the solids (RS). Toluene was added to each layer to dissolve bitumen. The solids separated from the toluene solution of the B layer will be referred to as bitumen layer solids (BS). The BS as well as A and RS fractions were repeatedly washed with aliquots of fresh toluene until the supernatant toluene solution was

Table 1 Compositions of oil sands

01	Oil sand composition (wt $\%$ )							
grade	Bitumen	Water	Solids					
High (I-1)	15.9	0.5	83.6					
Medium (II-1)	12.0	1.3	86.7					
Low (IV)	7.0	4.1	88.9					



Figure 1 Treatment scheme for oil sand

colourless. The solids of bitumen free layer A which will be referred to as AS, were flocculated using acetone.

#### Float-sink density fractionation

The BS fractions from the various grades of oil sand were fractionated in the density range from  $1.58 \text{ g cm}^{-3}$ (carbon tetrachloride) to 2.64 g cm<sup>-3</sup>. Liquids of density greater than  $1.58 \text{ g cm}^{-3}$  were obtained by mixing carbon tetrachloride and bromoform ( $d = 2.88 \text{ g cm}^{-3}$ ). The density fractionation procedure was as follows: to a known amount of BS ( $\approx 2 \text{ g}$ ) liquid of density 2.6 g cm<sup>-3</sup> was added ( $\approx 100 \text{ ml}$ ). Suspensions were mixed and then centrifuged for 1 h at 428 g. Floating material was collected from the surface of the suspension by suction, filtered, washed several times on the filter with acetone to remove traces of fluids used for density separation, dried and weighed. The procedure was repeated using fluids of densities 2.3, 1.9 and 1.6 g cm<sup>-3</sup>.

#### Humic and fulvic acids extraction

Samples of density separated solids were digested with 2% aqueous NaOH at 70°C. Digestion of solids with fresh NaOH solution was repeated weekly for five consecutive weeks. The procedure for humic and fulvic acids extraction is described in detail elsewhere<sup>5</sup>. The fulvic acids content was insufficient for any analysis to be performed. The humic acids suspensions were initially freeze-dried with the final moisture removal being carried out at room temperature in a vacuum desiccator over  $P_2O_5$ .

#### <sup>13</sup>C n.m.r.

Humic acids were dissolved in 0.5 N NaOH at a concentration of 50–100 mg ml<sup>-1</sup>. <sup>13</sup>C n.m.r. spectra were obtained on a Bruker MSL-300 spectrometer, set to

a sweepwidth of 50 kHz with inverse gated proton decoupling to suppress nuclear Overhauser effect (NOE). A pulse flip angle of  $45^{\circ}$  was used with a pulse repetition time of 2 s. As there were no sharp features in the spectra, the FIDs were truncated at 2 K before zerofilling to 8 K. Between 20000 and 50000 transients were collected to obtain an adequate signal to noise ratio.

#### Infrared analysis

Infrared spectra were recorded using a Perkin-Elmer model 683 i.r. spectrometer. Samples were run as KBr pellets.

#### Elemental analysis

The elemental analyses (C, H, N) were performed using a Perkin–Elmer model 240 CHN analyser. The insoluble organic carbon content (IOCC) of all solid fractions was obtained by subtracting carbonate carbon from the total carbon. Carbonate carbon was analysed titrimetrically after acid digestion using a Carbon Dioxide Coulometer Model 5010<sup>11</sup>. Total sulphur was analysed by a titrimetric oxygen flask combustion method, using a Schöniger type combustion apparatus<sup>12</sup>. Determinations of total sulphur, both organic and inorganic (pyrite, gypsum and/or iron sulphate) were made by X-ray fluorescence spectrometry using a PET crystal. There were no Fe lines interfering with the sulphur line of interest.

#### **RESULTS AND DISCUSSION**

As shown in our previous report<sup>6</sup>, oil sand solids could be separated into three fractions by the cold water agitation test (CWAT). These fractions differed markedly in their insoluble organic carbon content (IOCC) (Table 2). The solids separated from the bitumen layer designated as bitumen solids (BS) have the highest IOCC of 34.8-36.4%, followed by the solids isolated from an aqueous suspension (layer A) with IOCC of 5.4-5.9%, whereas the IOCC of the residual solids (RS) accounted for less than 0.3 wt %. To obtain more detailed information concerning the organic rich solids associated with bitumen, the BS fractions were subjected to density fractionation to separate them into 'free' organic matter organic matter complexed with inorganic and components. As a result four fractions were obtained for each BS of the three grades of oil sand. The range of the density fractions extended from 1.6 to  $2.6 \,\mathrm{g \, cm^{-3}}$ , respectively.

#### Elemental analysis of BS density fractions

The yield and elemental composition of the density fractions are given in *Table 3*. A decrease in C, H and N

Table 2 IOCC of BS, AS and RS fractions separated by CWAT

Oil sand sample	IOCC, wt % of dry bitumen free solids of various types					
	BS	AS	RS			
— I-1	34.75	5.40	0.03			
II-1	35.22	5.90	0.20			
IV	36.41	5.55	0.22			

 Table 3 Yield and elemental analysis of the BS density fractions

						Element	al analysis (%	alysis (%)					
01	Danita#	V:-14b		С	Н	N		S					
sand	$(g \text{ cm}^{-3})$	Yield <sup>b</sup> (wt %)	Total <sup>c</sup>	Inorg.			Org. <sup>d</sup>	Inorg. <sup>d</sup>	Total <sup>e</sup>	- Ash (%)			
I-1	1.6	20	57.50	0.19	4.3	1.1	1.38	0.31	1.6	3.8			
	1.9	20	43.81	0.63	3.4	0.9	1.06	0.37	1.8	30.8			
	2.3	35	36.83	2.30	2.6	0.7	0.71	0.58	1.8	52.9			
	2.6	20	8.60	2.05	0.6	0.1	0.61	3.61	4.1	75.2			
	> 2.6	5	3.70	1.40	0.5	0.0	n.s. <sup><i>f</i></sup>	n.s.	3.2	86.9			
II-1	1.6	20	56.20	0.43	4.1	1.1	n.s.	n.s.	2.9	8.0			
	1.9	30	45.22	0.36	3.3	0.9	n.s.	n.s.	2.3	32.1			
	2.3	30	23.11	0.48	1.8	0.4	n.s.	n.s.	2.7	63.5			
	2.6	15	6.15	0.52	0.5	0.1	n.s.	n.s.	0.0	85.6			
	>2.6	5	2.34	0.50	0.4	0.0	<b>n</b> . <b>s</b> .	n.s.	1.2	87.3			
IV	1.6	30	57.64	0.30	4.2	1.0	n.s.	n.s.	4.0	7.0			
	1.9	30	46.84	0.27	2.8	0.7	n.s.	n.s.	3.3	34.2			
	2.3	20	24.13	0.33	1.9	0.4	n.s.	n.s.	4.6	61.0			
	2.6	10	4.33	0.41	0.7	0.1	n.s.	n.s.	0.0	87.9			
	>2.6	10	1.90	0.35	0.5	0.0	n.s.	n.s.	1.4	89.1			

"Solids collected from the surfaces of liquids with indicated densities

<sup>b</sup>wt% is based on dry bitumen free BS

<sup>c</sup>Organic and inorganic

<sup>d</sup>X-ray fluorescence spectrometry

"Titrimetric oxygen flask combustion method

<sup>f</sup>Not sufficient sample



Figure 2 Density of various BS fractions versus wt% ash:  $\bigcirc$ , oil sand I-1;  $\bigcirc$ , oil sand II-1;  $\triangle$ , oil sand IV

concentration and an increase in ash content with increasing density is clear for all the BS fractions studied. For the one sample for which results were available (I-1) organic sulphur content also decreased with increase in density. Conversely, there is a trend for inorganic carbon and sulphur to increase with increase in ash content.

By plotting the density against the percentage ash and extrapolating to zero ash, densities of humic matter were estimated (*Figure 2*). It can be seen that they cover rather a narrow range from  $1.51-1.54 \text{ g cm}^{-3}$  indicating a similarity in humic matter present in different grades of oil sands.

The compositions of the density fractions on an ash free basis, atomic H/C, O/C, N/C, S/C ratios as well as densities (d) of humic matter calculated from the atomic volumes of the various atoms present as determined from elemental analysis are reported in *Table 4*. Densities were

calculated using the following equation proposed by van Krevelen<sup>13</sup>.

$$\frac{1200}{Cd} = 9.9 + 3.1 \frac{H}{C} + 3.7 \frac{O}{C} + 1.5 \frac{N}{C} + 14 \frac{S}{C} - \left(9.1 - 3.6 \frac{H}{C}\right) \frac{R}{C}$$
(1)

where R/C is the total number of rings per carbon atom. R/C was derived from the equation

$$f_{\rm a} = 2 - \frac{\rm H}{\rm C} - 2\frac{\rm R}{\rm C} \tag{2}$$

where  $f_a$  is aromaticity estimated by <sup>13</sup>C n.m.r.

Compositions and calculated densities of ash free BS fractions showed no definite trend and did not vary widely (*Table 4*), which is an indication of the similar nature of organic matter in each of these samples. There is a good correlation between the zero ash density (*Figure 2*) and the densities calculated on the basis of the results of elemental analysis.

#### Extraction of humic acid from density separated BS

Based on its solubility, humic matter can be subdivided into three main fractions: 1, fulvic acid which is soluble at both high and low pH; 2, humic acid which is soluble only at high pH and 3, humin, which is completely insoluble in alkaline aqueous solution. To analyse the distribution and structure of soluble portions of BS humic matter, fractions with densities 1.6 g cm<sup>-3</sup> and 2.6 g cm<sup>-3</sup> of high grade (I-1) and 1.6 g cm<sup>-3</sup> of low grade (IV) oil sand were extracted with 2 wt % NaOH solution. The wt % of humic acids isolated during each particular week of treatment *versus* extraction time is shown in *Figure 3*. It can be seen that the yield of humic acid per treatment was relatively constant during weeks 1 through 4 (although a slight decrease was observed after the first week for I-1 and II-1

Oil sand	Density <sup>a</sup> of BS fractions (g cm <sup>-3</sup> )		Elemental analysis (wt %, daf)						Atomic ratio				
		C	Н	N	O <sup><i>b</i></sup>	S	H/C	O/C	N/C	S/C	$(g \text{ cm}^{-3})$		
I-1	1.6	59.81	4.51	1.12	36.84	1.67	0.91	0.41	0.016	0.010	1.57		
	1.9	63.42	4.86	1.26	27.95	2.60	0.92	0.34	0.017	0.015	1.50		
	2.3	64.33	4.61	1.19	25.04	4.73	0.86	0.32	0.016	0.027	1.51		
II-1	1.6	61.11	4.45	1.24	30.01	3.15	0.87	0.37	0.017	0.019	1.56		
	1.9	66.40	4.80	1.39	21.81	4.50	0.87	0.27	0.018	0.025	1.47		
	2.3	63.42	4.92	1.25	23.33	4.89	0.92	0.28	0.016	0.028	1.50		
IV	1.6	67.71	4.89	1.18	21.50	4.70	0.87	0.32	0.015	0.026	1.42		
	1.9	66.00	5.02	1.16	22.04	5.02	0.91	0.25	0.015	0.029	1.46		
	2.3	61.84	4.79	0.89	22.05	6.70	0.93	0.27	0.012	0.041	1.52		

Table 4 Elemental analysis (daf), atomic ratios and calculated densities of organic matter present in different BS fractions

"Solids were collected from the surface of liquids with indicated densities

<sup>b</sup>By difference

<sup>e</sup>Method described in Ref. 9 has been used for calculations



**Figure 3** Yield of humic acid *versus* time of NaOH (2 wt %) solution treatment:  $\bigcirc$ , 1.6 g cm<sup>-3</sup> BS density fraction derived from oil sand I-1;  $\bigcirc$ , 2.6 g cm<sup>-3</sup> BS density fraction derived from oil sand I-1;  $\bigcirc$ , 1.6 g cm<sup>-3</sup> BS density fraction from oil sand IV

oil sand 1.6 g cm<sup>-3</sup> fractions) and then sharply decreased. Elemental analysis data of the humic acids extracted during the first and fourth weeks are given in *Table 5*. The ash contents of humic acids ranged from 2 wt % to 3 wt %.

In general humic acid elemental compositions did not change much with extraction time and were similar to the results reported previously for humic acids extracted from Athabasca oil sands<sup>5,14</sup>. It should be mentioned that the similarity in nitrogen content for humic acid and that for nearly ash free BS ( $1.6 \text{ g cm}^{-3}$  density fraction, *Table 4*) indicates that nitrogen does not originate from material adsorbed from bitumen as the nitrogen containing polar fraction of bitumen is not alkali soluble. The higher oxygen content of humic acid as compared with that of  $1.6 \text{ g cm}^{-3}$  density fractions of BS could be due to the fact that much of the polar material is not soluble in NaOH. Also humins that have lower oxygen content than humic acids, comprise a significant part of oil sand humic matter. Atomic H/C ratios for all humic acids were relatively low which could be an indication of condensed aromatic ring structures.

#### $^{13}C$ n.m.r. spectra of humic acid

Lately <sup>13</sup>C n.m.r. has been used extensively for structural analysis of humic matter derived from natural water, soils and coals<sup>15-24</sup>. However, there is no published information related to any n.m.r. study on humic substances isolated from different oil sands grades. The object of this work was first, to determine structural parameters for oil sand humic acids extracted from the 'free' organic matter  $(1.6 \,\mathrm{g}\,\mathrm{cm}^{-3}$  density fraction) as compared to those for humic acids derived from the fraction of density  $2.6 \,\mathrm{g}\,\mathrm{cm}^{-3}$ , and second, to compare n.m.r. characteristics of easily soluble humic matter (first week of extraction) with those for humic acids isolated during the fourth alkali treatment. Solution <sup>13</sup>C n.m.r. spectra of humic acid derived from the BS density fractions are presented in Figure 4. All spectra could be divided into five sections of chemical shift: 0 to 50 ppm (region I), aliphatic; 50 to 110 ppm (region II), N- and Osubstituted alkyl carbon, including carbohydrate, ether, amine, amide, alcohol, acetal, ketal, methoxyl functional groups; 110 to 160 ppm (region III), aromatic carbon.

Olefinic carbon which is not considered to be a major constituent of humic  $acids^{19}$  could also contribute to region III. This band can be subdivided into a band assigned to carbon bonded only to hydrogen or carbon (110–145 ppm) and a band assigned to O- and N-substituted carbon (145–160 ppm); 160 to 190 ppm, carboxyl, amide carbonyl, and ester carbonyl groups (region IV); 190 to 220 ppm, ketones and aldehydes (region V).

Assignments for chemical shifts in these regions<sup>19</sup> are given in *Table 6*. The percentage composition of the regions to the total spectra are shown in *Table 7*. The dominant signal in region I is observed at  $\approx 30$  ppm which is assigned to the carbon of polymethylene groups  $(CH_2)_n$ . The broad band of resonances present in the aliphatic region of all oil sand humic acids is an indication of a wide variety of carbon types (methyl, methylene and methine groups) being present. Area integration shows that paraffinic carbon content is in the range from 22 to 27% of total carbon. The spectral signals at approximately 55 ppm (region II) indicate the presence of

	Fractions Extraction density time (g cm <sup>-3</sup> ) (week) C <sup>c</sup> H		% daf"						
Oil sand		Extraction time (week)	C°	н	N	Sc	O <sup><i>b</i></sup>	Ash (%)	H/C ratio 0.84 0.85 0.87 0.79 0.82 0.89
I-1	1.6	1 4 <sup>d</sup>	59.1 59.6	4.2 4.2	1.2 1.1	2.1 1.9	33.5 33.1	2.3 2.2	0.84 0.85
I-1	2.6	1 4 <sup>d</sup>	60.6 64.7	4.4 4.3	1.2 1.0	1.7 1.8	32.1 28.2	2.5 3.0	0.87 0.79
IV	1.6	1 4 <sup>d</sup>	60.2 59.6	4.1 4.0	1.1 1.1	2.5 2.7	32.1 32.5	2.0 2.9	0.82 0.89

Table 5 Elemental analysis of humic acids derived from BS density fractions

<sup>a</sup>Dry ash free basis

<sup>b</sup>By difference

Organic + inorganic

<sup>d</sup>Fourth week of extraction (not cumulative)



**Figure 4** Solution <sup>13</sup>C n.m.r. spectra of humic acid separated from: a. oil sand I-1, 1.6 g cm<sup>-3</sup> density fraction, 1st week of extraction; b, as in a, 4th week of extraction; c, as in a, 2.6 g cm<sup>-3</sup> fraction; d, oil sand IV, 1.6 g cm<sup>-3</sup> BS density fraction 1st week of extraction; e, as in d, 4th week of extraction

methoxyl groups. These functional groups are likely characteristics of lignin residues which are usually associated with terrestrial (as opposed to marine) sources of organic matter. Weak signals observed at 60-72 ppm and 106 ppm suggest the presence of carbohydrates (polysaccharides), ethers, alcohols and amines. Region II carbon accounts for 10-17% of total carbon.

In region III a strong broad peak is observed at 130 ppm. Such resonances could be provided by unsubstituted and bridgehead aromatic carbons or olefinic nuclei. However, olefins are known to be present in negligible amounts in geological materials. Alkyl benzenes could also resonate in the 130 ppm region<sup>20</sup>. Area integration shows that 41-49% of the total carbon is aromatic. The presence of some phenolic and aryl alkyl ether carbons in region III is suggested by broad absorptions in the range 145-160 ppm. In region IV, relatively strong signals are centred around 175 ppm which is most likely that of carboxyl groups and amide carbon. In strongly alkaline solution phenolic carbon may also contribute to the spectral intensity in this region. Integration indicates that carbons in this area contribute from 9-15% to total carbon. The contribution from carbon in region V accounts for 4-6% of the total carbon.

The n.m.r. spectra in the 50–110 ppm, 145–160 ppm and 160–190 ppm regions are complemented by the infrared spectra (*Figure 5*, humic acid data derived from oil sand I-1, 1.6 g cm<sup>-3</sup> density fraction, 1st week of extraction. The i.r. spectra for the other humic acids were identical to that shown and hence they are not included). The presence of bonded carboxylic acids is suggested by a broad band in the region  $3600-2000 \text{ cm}^{-1}$  and by the peaks at 1710 and around  $1200 \text{ cm}^{-1}$ . Polymeric phenols, alcohols and chelated ketones could also be present as indicated by the bands at  $1710 \text{ cm}^{-1}$ ,  $1610 \text{ cm}^{-1}$  and the unresolved absorption between  $1800 \text{ and } 930 \text{ cm}^{-1}$ .

On the basis of the results showing the percentage composition of the regions to the total spectra (*Table 7*) the following conclusions have been drawn: the distribution of carbon type in each spectral region is similar for all oil sands humic acids and aromatic carbon is the predominant type of carbon for all samples. *Table 7* also shows that with increasing length of time of extraction with NaOH the areas in regions IV and V increase showing a greater presence of carboxyl.

Region I (0-50 ppm)	Region II (50–110 ppm)	Region III (110–160 ppm)	Region IV (160–190 ppm)	Region V (190-220 ppm)
			O II	O
Paraffinic C:CC'C	Alcohols C—OH	Olefinic-C	Carboxyl C–OH	Aldehyde C–H
c -				
(('('	Amines (C—NH <sub>2</sub> .NHR.C—NR <sub>2</sub> )	Aromatic-C	Ester C—OR	Ketone —C=O
C I			O II	
CC	Carbohydrates		Amide C—N	
Ċ	Ethers (CC)			
С—СН3	Methoxyl (OCH <sub>3</sub> )			
	Acetals (O—C—O)			

**Table 6**  $^{13}$ C-n.m.r. chemical-shift regions for various types of carbons present in humic substances

Table 7 Relative intensities for various regions of the <sup>13</sup>C n.m.r. spectra of oil sand humic acids

Oil sand		E trati	Total intensity (%)							
	density (g cm <sup>-3</sup> )	time (week)	I 0-50 ppm	11 50–110 ppm	111" 110–160 ppm	IV 160–190 ppm	V 190–220 ppm			
-1	1.6	1	26.8	10.1	48.1	11.4	3.5			
		4	22.8	17.1	41.2	13.3	5.6			
	2.6	1	23.6	13.9	49.0	9.2	4.1			
v	1.6	1	23.7	15.6	43.2	12.9	4.4			
		4	21.5	12.5	45.5	15.0	5.5			

<sup>a</sup>Percent of carbon in 110–160 ppm region to total carbon is used as a measure of aromaticity



Figure 5 Infrared spectrum of humic acid derived from oil sand I-1,  $1.6 \text{ g cm}^{-3}$  density fraction, 1st week of extraction

To better understand the origin of oil sand humic acids, it is instructive to compare their spectral characteristics with those for humic acids isolated from soil, peat, coal and marine environments. Humic substances are known<sup>15,17,19,20,23,24</sup> to be derived from two major sources of plant remains: namely, marine and terrestrial. Relatively mature terrestrial humic substances are mainly aromatic and contain methoxyl, hydroxyl, carboxyl and ether functional groups. The primary contributor to humic matter in many terrestrial sediments is lignin, which is a relatively non-biodegradable macromolecular substance, predominantly aromatic in structure, which occurs only in terrestrial vascular plants. In marine humic

acid, aliphatic structures appear to be a major characteristic. These structures are derived from microbial exudates or possibly algal lipids. It is believed<sup>19</sup> that due to such differences in structure it is possible to distinguish between humic matter of terrestrial and marine origin. In this respect aromaticity (per cent of carbon in 110-160 ppm region to total carbon) is considered to give a good indication of the relative contribution of terrestrial input to the sediment. It has been observed, for example, that in the case of marine humic acids, paraffinic structures are dominant and aromaticities are in the range 12-33%. Soil humic acids have aromaticities ranging from 21 to  $70\%^{15,17,19}$ . In humic acids derived from peat<sup>19</sup>, brown coal<sup>23</sup>, lignites and subbituminous coal<sup>24</sup> aromatic carbon accounts for 40-68%. A comparison between the aromaticity data presented in Table 7 and those reported in the literature suggests that humic acids derived from oil sand are largely terrestrial in origin, as are those isolated from soils, peats and coals.

It is usually accepted that petroleum generation is associated with type-I kerogen<sup>26</sup>. The presence of type-III kerogen closely associated with the bituminous sand is typical of the material that might have become attached to the mineral matter at or slightly before the time of sedimentation. The high oxygen content and relatively high percentage of extractable humic acids are indicative of a low level of geothermal maturation of this material.

#### CONCLUSIONS

By means of density fractionation, solids associated with bitumen (BS) derived from different grade oil sands, were separated into fractions having various humic matter (IOCC) content. The results for elemental analyses (daf) and calculated densities of humic matter extracted from different BS fractions, did not indicate significant differences in the nature of these materials. Some of the BS solids were subjected to NaOH treatment to extract humic acids. Elemental composition and <sup>13</sup>C n.m.r. structural parameters for humic acids extracted from 'free' organic matter  $(1.6 \,\mathrm{g}\,\mathrm{cm}^{-3}$  density fraction) and those for humic acids extracted from mineral concentrate  $(2.6 \,\mathrm{g}\,\mathrm{cm}^{-3}$  density fraction) were compared. Also the comparison was made between the properties of easily soluble humic matter (first week of extraction) and those for humic acids separated during the fourth NaOH treatment. For all humic acids analysed, elemental compositions as well as distribution of carbon types in each region of n.m.r. spectra were similar. It has been shown that aromatic carbon was the predominant type of carbon for all samples. Comparison between the aromaticity data for oil sand humic acids with those isolated from soils, peats and coals suggest that BS humic matter has a large terrestrial input.

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