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Characterization of minerals in oil sands by reflectance spectroscopy

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Diffuse-reflectance spectra (0.3–2.6 μm) of oil sands and mineral separates display a number of absorption bands which can be assigned to the spectrally significant minerals present in the samples. Minerals with strongly featured spectra such as kaolinite, illite and siderite can be identified even when they are minor constituents. Absorption bands in the 1.4 and 1.9 μm regions are most useful for identifying the presence and types of clay minerals, whereas the 1.0–1.2 μm region is most useful for identifying the presence of siderite.

Oil sands are a complex mixture of clays, bitumen (an array of various hydrocarbons), quartz grains, water and minor accessory minerals[1,2]. A detailed knowledge of the physical and chemical properties of these materials is essential for improving bitumen extraction processes and understanding the genesis and evolution of oil sand deposits[3]. A large number of analytical techniques have been applied to the study of oil sands because of their complex nature[4,5].

In the present work, the ultraviolet, visible and near-infrared diffuse spectral reflectance properties of oil sands have been examined in the laboratory in order to ascertain which physical and chemical properties of these materials are amenable to spectral detection and analysis. A total of 18 oil sand samples from the Athabasca deposit in northeastern Alberta, which span a range of bitumen contents as well as selected phase separates, were characterized by reflectance spectroscopy and X-ray diffractometry (XRD).

Diffuse reflectance spectroscopy (DRS) possesses a number of advantages over many other analytical techniques. Conventional infrared transmission spectroscopy requires extensive sample preparation which can alter the chemical and physical structure of oil sands[6]. Little or no sample preparation is required to yield usable diffuse reflectance spectra; consequently, the physical arrangement of the constituent phases can often be preserved and data can be acquired in near-real time. This is of particular importance in industrial process streams, where continuous monitoring of feedstocks may be required[7]. Some spectrometers are fully portable, allowing spectral data to be acquired in the field, such as on-site examination of drill cores, drill cuttings or outcrops. In addition, visible and near infrared spectroscopy can be used to study many liquid and amorphous phases and phases which occur in solid solution rather than as discrete mineral phases (unlike X-ray diffraction) and lighter elements such as C,

O, H and N which are not amenable to study by techniques such as electron microprobe analysis and X-ray fluorescence.

The ultraviolet, visible and near-infrared spectral regions are useful for detecting combinations and overtones of the various fundamental absorption bands found in the middle and far infrared spectral regions as well as crystal field transitions and charge transfer absorption bands[8–10]. These various types of absorption involve atomic processes acting over various distances, allowing the internal structure of a material to be examined at a number of scales. Perhaps the biggest drawback to DRS is the fact that information is obtained from, at best, the uppermost few millimetres of the material, the depth of examination being constrained by the optical density of the sample[11,12].

EXPERIMENTAL

The oil sand samples used in this study were obtained from the Syncrude Canada Ltd and Suncor Inc. leases near Fort McMurray, Alberta. Each sample was chopped by hand to minimize any inhomogeneities. Although this disturbed the physical structure of the material, it was necessary in order to obtain homogeneous duplicate samples for XRD and DRS analysis. A portion of each sample, ~2–3 g, was extracted in a micro-Soxhlet assembly using 10 × 50 mm cellulose thimbles and 10 ml of toluene. Extraction was completed in ~45 min. The solvent extract was transferred to a tared evaporating dish and allowed to dry overnight. Each dish was then weighed to obtain the bitumen content. The tared thimbles were dried at 100°C for 1 h before and after extraction and reweighed after extraction to obtain the solids content. This procedure was adopted to minimize analytical errors which could result from the liberation of water and volatile organics[13,14].

The extracted solids were ultrasonically disaggregated

and repeatedly wet-sieved with acetone to obtain well-sorted size fractions (<45 and $>45\,\mu$m). Both fractions were then characterized by XRD. The XRD data were acquired using a Rigaku X-ray diffractometer in the Department of Geology at the University of Alberta.

The reflectance spectra were acquired at the RELAB spectrometer facility at Brown University, Providence, RI. The spectra were measured in bidirectional reflectance mode ($i = 0°$, $e = 15°$) with 5 nm resolution. Details of the instrument are given in Pieters[15]. The sample spectra were measured relative to halon, a near-perfect diffuse reflector in the 0.3–2.6 μm region[16] and corrected for minor ($\sim 2\%$) irregularities in halon's absolute reflectance in the 2 μm region as well as for dark-current offsets. The reflectance spectra were processed using the Gaffey Spectrum Processing System, a personal-computer version of SPECPR[17].

Continuum removal was performed in some instances to isolate specific absorption bands. This was accomplished by dividing out a straight-line continuum tangent to the reflectance spectrum on either side of an absorption feature. Band centres and band minima were calculated by fitting a quadratic equation to $\sim$ 5–20 data points on

either side of a visually determined centre or minimum. Band depths (D_b) were calculated using Equation (32) of Clark and Roush[18].

RESULTS AND DISCUSSION

Both unextracted and extracted samples were spectrally characterized to determine whether the solids were measurably altered by the extraction process, whether the nature of the solids could be ascertained by spectral analysis in conjunction with XRD analysis, and whether the spectral signature of the solids could be detected in the unextracted sample spectra.

The reflectance spectra of representative low (<5 wt%), medium (5–10 wt%) and high (>10 wt%) bitumen-content oil sand spectra are shown in *Figure 1*. The compositional data for these samples are provided in
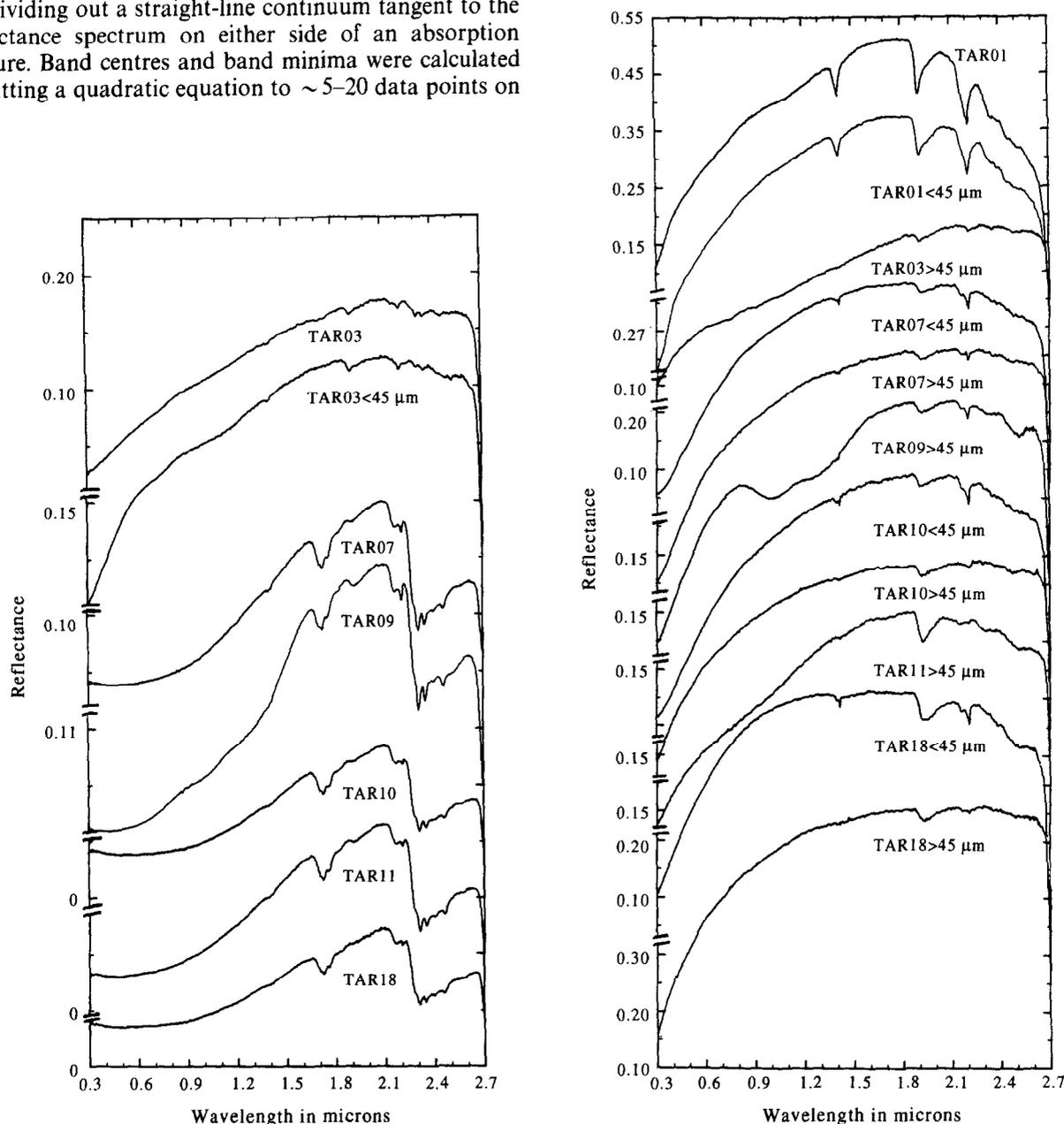
Figure 1 Reflectance spectra (0.3–2.6 μm) of Athabasca oil sands and bitumen-free fine-grained ($<45\,\mu$m) and coarse-grained ($>45\,\mu$m) fractions

Table 1. The results of the extraction process indicated that the errors in mass closure did not exceed 1.9%. The analytical data indicate that all the samples with the exception of TAR01 are composed predominantly of coarse-grained (>45 μm size) particles.

XRD analysis was used to determine relative approximate abundances of the mineral phases present in the fine-grained and coarse-grained fractions (*Table 2*). The shapes of the X-ray diffractograms in the low-angle regions suggested that the clay minerals display varying degrees of structural disorder.

The predominant solid phases present in Athabasca oil sands are quartz and clays. The latter are confined almost exclusively to the finer fraction, whereas quartz grains form the bulk of the coarser fraction[1]. The major clay species are kaolinite and illite, with lesser amounts of montmorillonite and chlorite[1].

Clay minerals

Clays exhibit a number of absorption bands in the 0.3–2.6 μm region, particularly near 1.4 and 1.9 μm and between 2.1 and 2.6 μm[19–21]. The bands near 1.4 μm are due to OH fundamental overtones of structural OH and bound water, whereas the bands near 1.9 μm are due to bound water. The bands in the 2.1–2.6 μm region are due to various ligand–OH combination bands. If the bonding ligand is Al the strongest bands appear near 2.2 and 2.3 μm; Mg–OH bands appear most prominently near 2.3 and 2.4 μm[19]. Pure quartz shows no absorption

Table 1 Composition of oil sand samples

Sample	<45 μm grain size (wt%)	>45 μm grain size (wt%)	Bitumen (wt%)	Total (wt%)
TAR01	97.1	0.8	0.2	98.1
TAR03	24.3	71.0	3.8	99.1
TAR07	14.2	72.2	12.9	99.3
TAR09	5.8	84.3	9.4	99.5
TAR10	12.7	77.6	9.0	99.3
TAR11	3.9	82.1	13.0	99.0
TAR18	1.7	83.2	14.6	99.5

Table 2 Mineral phases identified in oil sands by XRD[a]

Sample	Size fraction (μm)	Major constituents	Minor constituents	Trace constituents
TAR01	>45	Q	P,S	G
	<45	Q	I,K	–
TAR03	>45	Q	–	D,I
	<45	Q	K,I	M,C
TAR07	>45	Q	–	–
	<45	Q	K	I,S,C
TAR09	>45	Q	S,D	–
	<45	Q,S	D,K	I
TAR10	>45	Q	–	–
	<45	Q	K,I	S
TAR11	>45	Q	–	I
	<45	Q	K	I,C
TAR18	>45	Q	–	I
	<45	Q	K	I,D

[a] C = calcite; D = dolomite; G = graphite; I = illite; K = kaolinite; M = marcasite; P = pyrite; Q = quartz; S = siderite

Table 3 Absorption band positions near 1.4 and 1.9 μm[a]

Sample	Sample type	Band positions near 1.4 μm	Band positions near 1.9 μm
TAR01	unextracted	(1.397), (1.405), 1.414	1.907
	<45 μm	(1.397), (1.405), 1.412	1.907
TAR03	unextracted	(1.395), 1.405, 1.415	1.909, 1.935, 1.955
	>45 μm	1.400, 1.415	1.909, 1.930, 1.960
	<45 μm	(1.395), 1.406, (1.415)	1.910, 1.935, 1.950
TAR07	unextracted	1.396, 1.405, 1.414	1.908, 1.920, 1.942
	>45 μm	(1.395), 1.400, 1.414	1.919, 1.940
	<45 μm	1.397, (1.402), 1.414	1.915, 1.935
TAR09	unextracted	1.397, (1.402), 1.414	(1.910), 1.930, 1.940
	>45 μm	1.395, (1.402), 1.414	1.907, 1.923, 1.940
TAR10	unextracted	1.395, (1.402), 1.414	1.906, 1.924
	>45 μm	1.407, 1.414	1.913, 1.932
	<45 μm	1.397, 1.414	1.906, 1.915
TAR11	unextracted	1.395, 1.405, 1.415	1.910, 1.930
	>45 μm	1.407, 1.415	1.918
TAR18	unextracted	(1.393), 1.405, 1.416	1.906, 1.934
	>45 μm	1.403, 1.415	(1.907), 1.922, 1.932
	<45 μm	1.396, 1.414	1.921, 1.936

[a] Figures in parentheses denote a shoulder on a more prominent band

bands in the 0.3–2.6 μm region but may display weak absorption bands near 1.4 and 1.9 μm due to water contained in fluid inclusions[19].

Of the predominant clay species found in Athabasca oil sands, kaolinite displays two prominent absorption bands near 1.38 and 1.42 μm (due to the availability of two structural sites for OH), a weak bound-water absorption band near 1.9 μm (due to its low adsorptivity) and a series of absorption bands in the 2.1–2.6 μm region with the most prominent found near 2.16 and 2.20 μm. Illite spectra display absorption bands near 1.42, 1.92, 2.22 and 2.36 μm which are generally weaker than those of kaolinite[20,22]. Free water exhibits absorption bands near 1.45 and 1.94 μm[23–25]. The clay absorption bands near 1.4 and 1.9 μm are particularly important in oil sands spectral analysis because they are not significantly overlapped by bitumen absorption bands, which are generally confined to the 1.7 and 2.2–2.6 μm regions[13,14,26].

Comparison of selected unextracted and extracted sample spectra indicates that the presence of bitumen results in a decrease in overall reflectance and the appearance of absorption bands in the 1.7 and 2.2–2.6 μm regions. The extracted-fraction spectra almost invariably exhibit absorption bands in the 1.4, 1.9 and 2.2–2.6 μm regions (*Figure 1*).

The bitumen extraction process and subsequent sample preparation, which include wetting and drying, result in changes in the shapes of absorption bands associated with clay minerals. Heating generally reduces hydroxyl-associated band depths, whereas wetting generally increases their depths[20] as well as altering band shapes. This effect is particularly evident in the 1.4 μm region of the unextracted versus extracted fine-grained fractions of samples TAR01, TAR07 and TAR10 (*Figure 2*). In spite of these changes, the spectrally dominant clay species (kaolinite) can still be identified by the presence of two closely spaced absorption bands near 1.4 μm. The appearance of these bands may be modified by the bitumen extraction process, but they retain their overall characteristic shape.

The spectral variations seen in the 1.4 μm region among different extracted-sample spectra suggest that
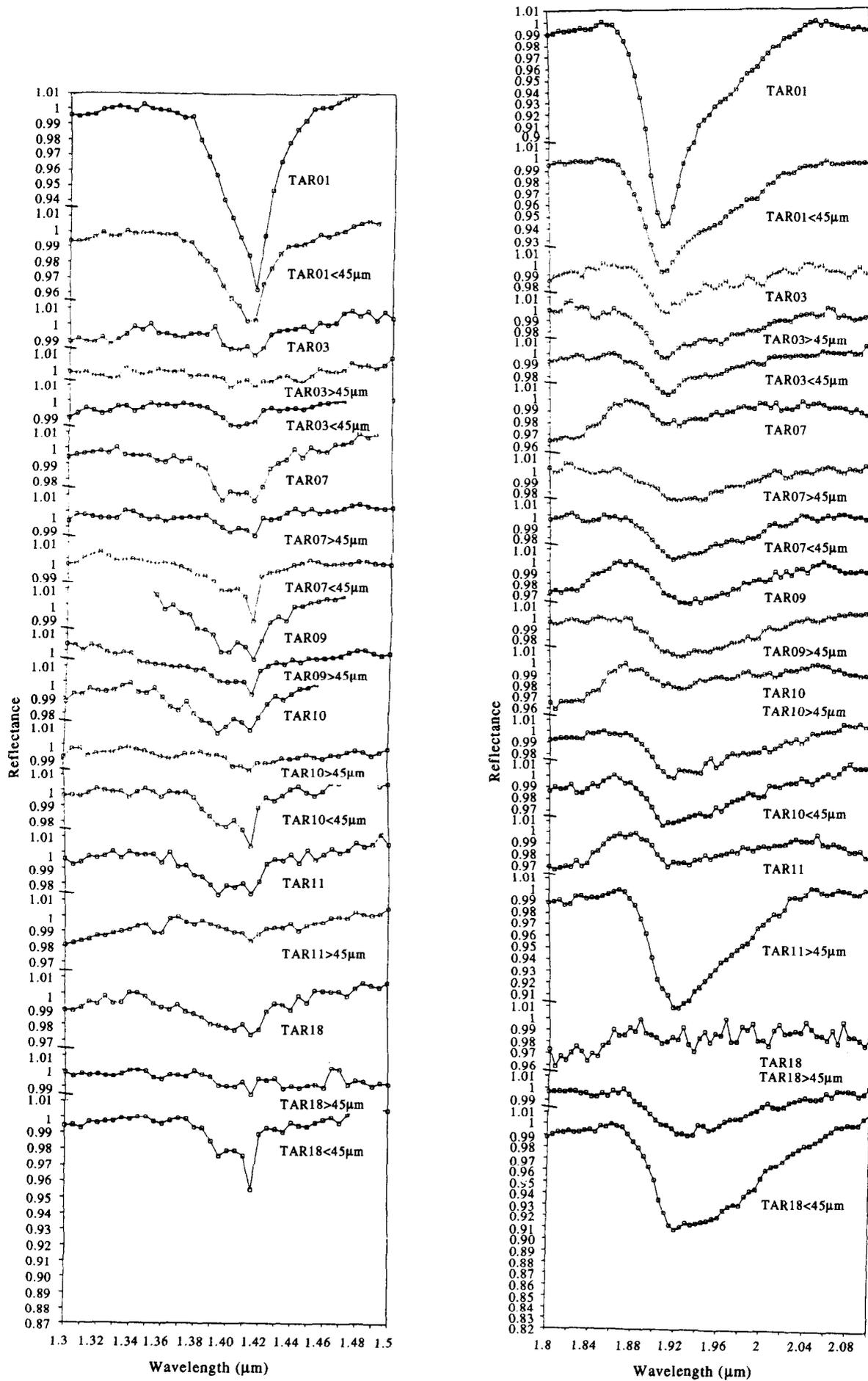
Figure 2 Continuum-removed reflectance spectra of oil sands and bitumen-free separates in the 1.4 and 1.9 μm regions

Table 4 Maximum band depths in the 1.4 and 1.9 μm regions

Sample	Sample type	Band depth (%) near 1.4 μm	Band depth (%) near 1.9 μm
TAR01	unextracted	11.8	17.8
	<45 μm	5.6	9.8
TAR03	unextracted	2.1	4.4
	>45 μm	0.9	4.3
	<45 μm	1.2	3.7
TAR07	unextracted	3.3	2.2
	>45 μm	1.5	2.8
	<45 μm	3.9	3.7
TAR09	unextracted	3.5	3.8
	>45 μm	2.2	3.4
TAR10	unextracted	2.7	2.2
	>45 μm	1.2	4.2
	<45 μm	3.9	4.6
TAR11	unextracted	2.8	2.8
	>45 μm	1.3	10.3
TAR18	unextracted	2.7	2.7
	>45 μm	1.7	3.7
	<45 μm	4.5	9.4

different proportions of various hydrated minerals are contributing to the spectrum in this region and/or the hydrated minerals vary structurally between samples. Most of the unextracted-sample spectra exhibit the two closely spaced absorption bands in the 1.4 μm region which are characteristic of kaolinite (*Table 3*). This is not unexpected, given the fact that kaolinite is more strongly featured than illite, and also accords with the XRD data.

It is expected that the clay minerals would be concentrated in the finest fraction. This is evident from both the XRD and spectral data. The 1.4 μm absorption bands are deeper in the finer-fraction spectra (with the exceptions of the most bitumen-poor samples), followed by the unextracted spectra and the coarse-grained spectra (*Table 3*). The fine-grained sample spectra show a more kaolinite-like spectrum in the 1.4 μm region than either the coarse-grained or unextracted-sample spectra (*Figure 2*). The smaller band depths in the unextracted-sample spectra than in those of the extracted fractions are largely due to the presence of the bitumen, which, by analogy to other dark phases, reduces band depths[27,28]. The fact that the 1.4 μm band depths are greatest for the fine-grained fractions, which in most cases form <50% of the sample, indicates that the clay minerals are spectrally dominant in this region.

The absorption bands in the 1.9 μm region are attributable to bound water but not structural OH[19]. For samples containing more than a few weight per cent bitumen, the deepest absorption bands in this region are present in the fine-grained extracted-sample spectra, followed by the coarse-grained extracted fraction and the unextracted bulk samples (*Table 4*). This sequence indicates that the clays are also spectrally dominant and that bitumen also reduces band depths in this wavelength region.

The 2.1–2.6 μm region is the preferred region for spectral identification of clays outside the middle and far infrared regions[29]. Unfortunately this region also contains the most intense bitumen combination and overtone bands, which leads to complex spectral interferences between the various phases[30]. The most bitumen-poor samples, TAR01 and TAR03, are composed

predominantly of fine-grained minerals which include clays. Bitumen absorption bands for these samples (*Figure 1*), based on the appearance of absorption bands near 1.7 μm and comparisons with the extracted-sample spectra, are essentially absent (TAR01) or weak (TAR03). In addition, the structural heterogeneity of clays among the various samples is evident from the spectral differences between the fine-grained extracted-sample spectra.

Absorption bands in the TAR01 sample are found near 2.205, 2.357, 2.39 and 2.445 μm, with an additional absorption band possibly present near 2.165 μm appearing as a shoulder on the main absorption band. These values are characteristic of both kaolinite and illite[19–22,29]. These two minerals are present in subequal amounts, and in spite of the fact that illite is more weakly featured than kaolinite, both clay species can be recognized in the 2.1–2.6 μm region of all the fine-grained extracted-sample spectra.

The decrease in reflectance on the shorter-wavelength side of ~1.8 μm seen in the fine-grained extracted-sample spectra is more intense than that seen in the spectra of 'clean' kaolinites and illites[19–22,29,31]. The reflectance reduction is probably due to the presence of small amounts of iron and/or residual interstitial bitumen in the fine grained minerals[1,32–35].

Quartz

Both the coarse-grained and fine-grained extracted fractions of the various oil sands are composed predominantly of quartz, as expected[36] (*Table 2*). The reflectance spectra of the >45 μm size fractions (*Figure 1*) are relatively featureless and are characterized by a gradual increase in reflectance towards longer wavelengths and weak absorption bands near 1.4 and 1.9 μm (*Figure 2*), similar to impure quartz spectra[19]. This spectral behaviour is also consistent with the XRD data, which indicate that quartz is the dominant phase in the coarser fractions (*Table 1*). The weak hydroxyl bands seen in the coarse-grained fraction spectra are probably associated with the quartz, since XRD analysis reveals that these samples are composed almost exclusively of quartz.

Siderite

XRD analysis of the TAR09 sample indicates that in addition to quartz, carbonate minerals (particularly siderite) are present in measurable amounts (*Table 2*). The reflectance spectrum of the extracted fraction (*Figure 1*) is unlike the other sample spectra in that it exhibits a broad absorption feature in the 1.0–1.2 μm spectral region. This feature is commonly associated with ferrous iron and closely resembles the reflectance spectrum of siderite[37]. This feature is not as prominent in the unextracted sample spectrum, but the weak inflections present near 1 and 1.2 μm are suggestive of siderite absorption bands. In addition, the strongest carbonate absorption band (found near 2.53 μm) is also present in the TAR09 spectrum (*Figure 1*).

Pyrite

A small amount of pyrite is present in the coarse-grained fraction of TAR01. Unfortunately, not enough of this sample was available for spectral reflectance measurements. In any case, pyrite shows only weak

absorption bands in the 0.3–2.6 μm region and is not expected to be spectrally detectable when it is only a minor constituent[38].

Dark grains

The extracted fractions of some of the samples, particularly TAR03 and TAR11, contain a few to several per cent of dark-coloured grains in both the fine- and coarse-grained fractions. Qualitative electron microprobe analysis of some of these dark grains indicates that they are composed predominantly of Al and Si, with lesser amounts of Fe and Ni, and may be related to previously identified humic–inorganic matter complexes[32–34].

CONCLUSIONS

Visible and near-infrared reflectance spectra of oil sands exhibit numerous absorption features which are attributable to the various constituent mineral phases. The presence of bitumen reduces both overall reflectance and band depths but generally does not completely suppress mineral absorption bands. Absorption bands attributable to both major and minor constituent minerals such as quartz, clays and siderite can be recognized in both bitumen-bearing and bitumen-free sample spectra. The bitumen extraction and sample preparation procedures can lead to changes in band shapes and positions of absorption bands associated with bound and structural water, i.e. clays. Nevertheless the spectrally dominant clay species in bitumen-extracted sample spectra can be identified in almost all instances.

The abundance of well-defined mineral absorption bands in oil sand spectra, coupled with the normally minimal sample preparation requirements of reflectance spectroscopy, suggests that this analytical technique can be developed for the rapid characterization of minerals present in oil sands. These studies are being expanded to attempt to quantify some of the spectral–compositional relations outlined above.

ACKNOWLEDGEMENTS

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