CLAY-HYDROCARBON MIXTURES: SPECTRAL PROPERTIES AND IMPLICATIONS FOR REMOTE SENSING IDENTIFICATION OF ORGANIC-BEARING SURFACES; Edward A. Cloutis, Department of Geology, University of Alberta, Edmonton, Alberta T6G 2E3

Introduction: Positive identification of extraterrestrial occurrences of organic material has important implications for models of the origin and evolution of the solar system and for life on earth. The ultraviolet, visible, and near-infrared spectral reflectance properties of one group of geologically significant hydrocarbons, oil sands, have been examined in order to identify the spectral features in the 0.3- to 2.6-μm spectral region which are characteristic of the organic phases. Oil sands were chosen for spectral analysis because they contain appreciable quantities of bitumen and clay, in addition to quartz sand which is spectrally neutral [1,2]. In this sense they are similar to CI and CM carbonaceous chondrites [3,4].

Results: A suite of oil sand samples from the Athabasca deposit located in north eastern Alberta were spectrally characterized. The samples contain between 0 and 15 wt. % bitumen, and this range has been subdivided into three groups to facilitate spectral interpretation: 0-5 wt. % (low), 5-10 wt. % (medium), and 10-15 wt. % (high). A representative member of each group was selected for more detailed spectral analysis. Organic absorption band assignments in the 0.3- to 2.6-μm region have been made on the basis of infrared transmission spectra of oil sands and other materials. Table 1 lists the most intense fundamental absorption bands in the 3800-1000 cm^{-1} region [5,6,7]. As expected, all these bands involve various stretching and bending excitations of carbon-bearing molecules. In addition to these discrete bands, bitumen shows a region of moderately intense absorption between ~1750 and ~900 cm^{-1} which can contribute to absorption bands in the 2.2- to 2.6-μm region through various first order overtones and combinations.

The predicted positions of the various binary combinations and first order overtones of the fundamental absorption bands are listed in Table 2. They generally cluster into two wavelength regions- near 1.7μm and between 2.2 and 2.6μm. Higher order overtones and more complex combination bands are not considered here as the intent is to examine only the most intense possible bands.

Low bitumen content group: Oil sand sample 82-05 contains 3.2 wt. % bitumen (Table 3). Its reflectance spectrum is shown in Figure 1. In spite of the low overall reflectance it displays a number of absorption bands. The bands near 1.4 and 1.9μm can be attributed to clay lattice-OH and free water absorptions [2,8,9,10]. The width and shape of the 1.9μm band suggests that the clays are structurally disordered and/or that structural and bound water are incorporated into a number of distinct sites. Both hypotheses are supported by other observational data [1]. The 2.3- to 2.6μm region shows a gradual decline in reflectance which is characteristic of clays [2,8,9,11] and its appearance is consistent with the two major types of clays present in oil sands, kaolinite and illite [2,8,9,11]. The expected organic absorption bands near 1.7μm are almost indistinguishable and the appearance of the 2.2-2.6μm interval does not require the presence of organics. The only indirect evidence for bitumen is the low reflectance which is atypical of clays [2,8,11].

Medium bitumen content group: Sample 87-04 contains 8.1 % bitumen (Table 3) and its reflectance spectrum is shown in Figure 2. This spectrum exhibits absorption bands due to clay and water (near 1.4 and 1.9μm) and bitumen (near 1.7μm). In addition, the appearance of the 2.2-2.6μm region differs markedly from that of Figure 1. Absorption in the 2.3-2.6μm interval is more intense and there is no reflectance decline towards the longer wavelengths, likely due to the higher organic content. The complex shape of the 1.7μm feature suggests that a number of molecular species are contributing to this wavelength region. The most intense regions of near-infrared absorption, 2.31 and 2.35μm, correlate with CH_2 and CH_3 stretching and bending combinations and overtones. More detailed examination of these wavelength regions is planned to permit the identification of specific molecular species.

High bitumen content group: The representative sample of this group, #86-19, contains 13.2 wt. % bitumen (Table 3). Its reflectance spectrum (Figure 4) is dominated by hydrocarbon absorption bands. The 1.4 and 1.9μm clay/water bands are virtually absent. Again, the 1.7μm region appears to contain a number of overlapping absorption bands and intense bands are present at 2.31 and 2.35μm. The higher bitumen content is probably responsible for the positive slope in the 2.3-2.6μm interval.

Discussion: The three oil sand spectral groups have been constructed merely as an aid to the identification of spectral features. There are no abrupt changes in spectral properties, only gradual variations. Of most interest are the various spectral features associated with the organic fraction. The 1.7μm spectral region is a fruitful area for detecting hydrocarbons because, unlike the 2.3-2.6μm region, it is not overlapped by clay absorption bands. At bitumen abundances of 3 wt. % this band is marginally resolvable, at 8 wt. % clearly resolvable, and at 13 wt. % dominates the lower wavelength region. The organic absorption bands in the 2.3-2.6μm region are more prominent but are overlapped by the various clay-lattice bands. Even so, absorption bands can be resolved at 2.31 and 2.35μm. As bitumen content increases, the 2.3-2.6μm interval aquires an increasingly positive slope and shows more intense absorption. The infrared region of moderate absorption (~1750 to ~900 cm^{-1}) is largely responsible for this and only the most intense combination and overtone bands are resolvable against this low albedo "continuum". Clearly, the most promising short wavelength regions for hydrocarbon detection are near 1.7μm and between 2.3 and 2.6μm.

Organic absorption features have been tentatively identified on some extraterrestrial bodies on the basis of detection of fundamental organic absorption bands near 3.4μm [12,13]. Because solar flux is greater at shorter wavelengths, examination of shorter wavelength regions, particularly near 1.7μm should be easier to accomplish and provide additional evidence for or against the existence of surficial hydrocarbons.

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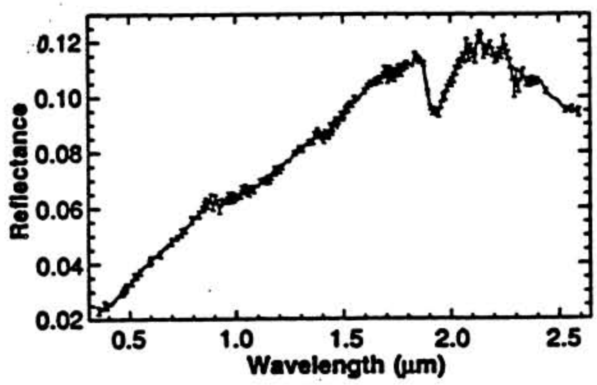

Figure 1. Diffuse reflectance spectrum of low bitumen content (3.2 wt. %) sample 82-05.

BAND	FUNDAMENTAL FREQUENCY (Inverse cm)	ASSIGNMENT
a	3030	alkene, aromatic C-H stretch
b	2950	asymmetric CH_3 stretch
c	2920	asymmetric CH_2 stretch
d	2875	symmetric CH_3 stretch
e	2850	symmetric CH_2 stretch
f	1700	carbonyl/carboxyl C-O stretch
g	1600	aromatic carbon stretch
h	1450	asymmetric CH_2, CH_3 bend
i	1375	symmetric CH_3 bend

Table 1. Energies of the most intense fundamental hydrocarbon absorption bands (cm^{-1}).

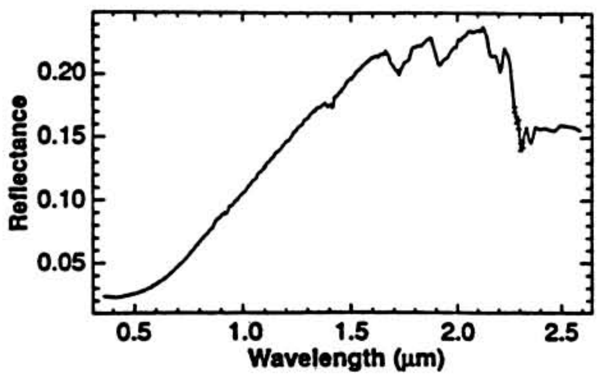

Figure 2. Diffuse reflectance spectrum of medium bitumen content (8.1 wt. %) sample 87-04.

COMBINATION AND OVERTONE BANDS

Combination/ Overtone Band	Wavelength (microns)	Combination/ Overtone Band	Wavelength (microns)
2a	1.650	e+f	2.198
a+c	1.681	c+g	2.212
2b	1.695	e+g	2.247
a+e	1.701	b+h	2.273
2c	1.712	c+h	2.288
b+d	1.717	b+i, d+h	2.312
c+e	1.733	e+h	2.326
2d	1.739	d+i	2.353
2e	1.754	c+j	2.532

Table 2. Predicted wavelength positions of combinations and overtones of the hydrocarbon absorption bands listed in Table 1.

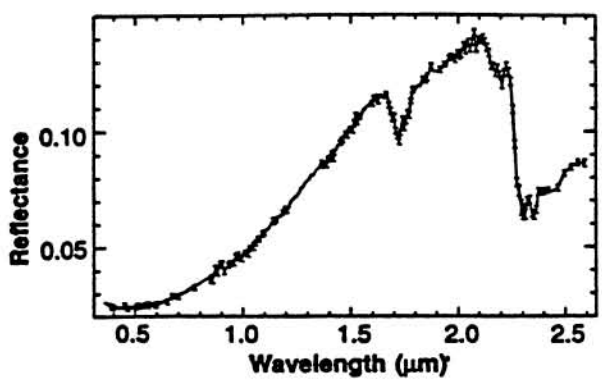

Figure 3. Diffuse reflectance spectrum of high bitumen content (13.2 wt. %) sample 86-19.

Sample No.	82-05	87-04	86-19
Bitumen (Wt. %)	3.2	8.1	13.2
Water (Wt. %)	8.1	6.6	2.5
Solids (Wt. %)	88.7	85.3	83.9
<400 mesh (Wt. %)	32.1	29.3	6.0
>400 mesh (Wt. %)	67.9	70.7	94.0

Table 3. Bitumen, water, and solids abundances of the various oil sand samples.