Spectral Reflectance Properties of Carbon-Bearing Materials

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The 0.3-2.6 μm spectral reflectance properties of carbon polymorphs (graphite, carbon black, diamond), carbides (silicon carbide, cementite), and macromolecular organic-bearing materials (coal, coal tar extract, oil sand, oil shale) are found to vary from sample to sample and among groups. The carbon polymorphs are readily distinguishable on the basis of their visible-near infrared spectral slopes and shapes. The spectra of macromolecular organic-bearing materials show increases in reflectance toward longer wavelengths, exceeding the reflectance rise of more carbon-rich materials. Reflectance spectra of carbonaceous materials are affected by the crystal structure, composition, and degree of order/disorder of the samples. The characteristic spectral properties can potentially be exploited to identify individual carbonaceous grains in meteorites (as separates or in situ) or to conduct remote sensing geothermometry and identification of carbonaceous phases on asteroids. © 1994 Academic Press, Inc.

INTRODUCTION

The carbon-bearing phases present in many classes of meteorites have received an inordinate amount of attention given their generally low abundances (<5 wt%). The application of visible and near infrared spectroscopy to analysis of these phases has generally lagged behind the application of other analytical techniques. Spectroscopy possesses a number of advantages over other more commonly employed analytical techniques. It is capable of providing structural and compositional information concerning amorphous or poorly crystalline phases which are not amenable to X ray diffraction analysis (e.g., Singer 1985) or phases containing low atomic weight elements which are not amenable to electron microprobe analysis (Pella 1986).

Meteoritic carbon-bearing phases are of interest because (1) they are potentially useful cosmothermometers which can provide information concerning preaccretionary nebular conditions and postaccretionary metamorphism (Mueller 1953, Kerridge 1985, Rietmeijer and Mackinnon 1985a, 1985b, Wright et al. 1990), (2) they can contain isotopically "anomalous" element abundances which may reflect presolar nebular conditions (Bernatowicz et al. 1987, Zinner et al. 1987, Anders 1988, Blake et al. 1988, Zinner 1988, Amari et al. 1990), (3) they are the main carriers of primordial noble gases (Weber et al. 1971, 1976, Fukunaga et al. 1987, Matsuda et al. 1991) and (4) they can strongly affect the spectral signatures of more abundant minerals with which they are intimately associated in carbonaceous chondrites and ureilites (Johnson and Fanale 1973, Salisbury et al. 1975, Gaffey 1976, Gaffey and McCord 1979, Larson et al. 1979, Wagner et al. 1987, Moroz and Pieters 1991).

The term carbonaceous chondrites is used throughout the text to refer to meteorites which are generally regarded as chondrites regardless of whether they contain chondrules. This convention, although not completely accurate, is widely used (e.g., Wasson 1974, Kerridge and Matthews 1988).

Interplanetary dust particles (IDPs) have been studied by a number of techniques including infrared spectroscopy (Fraundorf et al. 1983, Sandford and Walker 1985, Sandford 1986). A number of them contain carbon-bearing phases as a major component (e.g., Allamandola et al. 1987, Blanford et al. 1988) in sufficient abundance to impart an overall black color to the grains (Brownlee et al. 1980, Wopenka 1988). This carbonaceous material has yet to be fully characterized but seems to comprise a number
of distinct phases including amorphous carbon, poorly graphitized carbon, turbostratic carbon, polycyclic aromatic hydrocarbons (PAHs), "kerogen-like" compounds, iron carbides, lonsdaleite, and various other hydrocarbons (Knacke 1977, di Brozolo et al. 1985, McKay et al. 1985, Christofferson and Buseck 1986, Rietmeijer and Mackinnon 1987, Wopenski 1988, Gibson and Hartmetz 1991, Gibson 1992). The carbonaceous phases in IDPs are of interest because they contain a number of isotopic anomalies (McKeegan et al. 1985, Gibson 1992 and references therein) and may be useful cosmothermometers (Rietmeijer and Mackinnon 1985a,b, Nuth 1990). Improvements in our analysis of these materials are essential if recently discovered extensive terrestrial deposits of IDPs are to be fully exploited (Murrell et al. 1980, Mackinnon 1987, Maurette et al. 1987).

A number of asteroid classes, including the B, C, D, F, G, P, and T classes, are characterized by low albedos (<~10%) and relatively featureless reflectance spectra (Tholen 1984, Tholen and Bell 1987, Gaffey et al. 1989). These spectral characteristics and cosmochemical considerations have led a number of investigators to suggest that carbon-bearing phases are responsible for the low albedo and general lack of mineral absorption features in their reflectance spectra (e.g., Hartmann et al. 1982, Jones et al. 1990). However, the direct identification of carbonaceous material on asteroids is both rare and generally tenuous (Cruikshank and Brown 1987, Piscitelli et al. 1988, Cruikshank et al. 1990). If carbon-bearing phases are present on asteroid surfaces, changes in the composition, abundance, and structure of these phases may account for the variety of slopes seen in asteroid spectra with changes in heliocentric distance (Gradie and Tedesco 1982, Hartmann et al. 1987, Cruikshank 1989, Jones et al. 1990, Mueller et al. 1992) and the slopes of cometary nuclei spectra (Hanner et al. 1985, Brooke and Knacke 1986, Weissman et al. 1989).

The 0.3–2.6 μm reflectance spectra of a variety of carbon polymorphs, carbides, and macromolecular carbon-bearing materials have been examined in order to attempt to unravel the physical and chemical properties which affect the spectra. Improved understanding of the compositional-spectral relationships should permit improvements in characterizing carbonaceous phases in meteorites, IDPs and asteroids. This information can in turn be applied to constraining pre- and postaccretionary processes which have affected these objects.

**EXPERIMENTAL PROCEDURE**

Both natural and synthetic samples have been used and are grouped into carbon polymorphs, carbides, and macromolecular organic-bearing classes. The carbon polymorphs include natural graphite from Sri Lanka (GRP101, <45-μm grain size), synthetic "amorphous" graphite (GRP102, <45-μm grain size), synthetic carbon black (LCA101, <0.021-μm grain size), and natural diamond (DIA101, <1-μm grain size). The carbides include synthetic silicon carbide (SiC) in two grain sizes from different sources (SIC101, <37-μm grain size; SIC102, 7-μm grain size) and synthetic cementite (Fe3C) (CEM101, <45-μm grain size). The macromolecular organic-bearing phases were selected on the basis of their compositional complexity and abundance of aromatic organics and include bituminous coal from Frank, Alberta (COAL01, <37-μm grain size), coal tar extract (<37-μm grain size), oil sand from the vicinity of Fort McMurray, Alberta (TAR17, unsorted) and oil shale from the vicinity of Rifle, Colorado (OILS10, <45-μm grain size).

Most of the samples were obtained in powdered form. Those that were not were crushed in an alumina mortar and pestle. Impurities were removed through a combination of hand picking and magnetic separation. All samples were dry sieved in order to minimize inadvertent chemical and structural alterations of the materials. The samples were characterized by X-ray diffraction (XRD) analysis to determine relative degrees of order/disorder on the basis of relative peak heights, widths, and low angle scattering (Biscoe and Warren 1942, French 1964, Griffin 1967, Oberlin et al. 1980), for identifying the presence of any undesirable accessory phases, and for identifying the crystalline mineral phases present in the coal, oil shale, and oil sand samples.

Bidirectional reflectance spectra have been measured at the Reflectance Experiment Laboratory (RELAB) spectrometer facility in the Department of Geological Sciences at Brown University (Pieters 1983). The data were acquired at i=0°, ε=15°, and 5-nm resolution relative to halon, which is a near-perfect diffuse reflector in the 0.3- to 2.6-μm range (Weidner and Hsia 1981). The spectra have been corrected for minor irregularities in halon’s absolute reflectance in the 2-μm region, as well as for dark current offsets. The terms red slope and blue slope are used throughout the ensuing discussion. Red slope indicates that reflectance generally increases toward longer wavelengths while blue slope indicates that reflectance generally decreases toward longer wavelengths.

**RESULTS**

Analysis of carbon-bearing materials in meteorites has been hampered by difficulties in isolating them and the lack of satisfactory methods for characterizing them in the solid state (Kitajima and Masuda 1992). In addition, commonly employed separation/concentration processes may cause undesirable compositional changes in carbonaceous materials (Murase 1992). The spectrally characterized samples have been divided into the three groups...
Carbon black is relevant to studies of carbonaceous phases in meteorites because a portion of the carbon in carbonaceous chondrites and to a lesser extent in ureilites is present in poorly crystalline and/or amorphous forms (Barber 1985, Wacker 1986, Wright et al. 1990, Kagi et al. 1991). XRD analysis of the carbon black sample indicates that it is largely amorphous with a broad, diffuse peak near 3.7 Å and extensive low angle scattering.

The reflectance spectrum of the carbon black sample (LCA101) is shown in Fig. 1. It exhibits low overall reflectance (<1.2%) and a shallow reflectance minimum in the 1.4- to 1.7-μm region but is otherwise relatively featureless. Reflectance and photoacoustic spectra of other carbon black samples (Johnson and Fanale 1973, Gradie and Veverka 1980, Vidrine 1980, Lochmuller et al. 1981, Cruikshank 1987) are similar to the carbon black spectrum in Fig. 1: generally featureless with a slightly blue sloped spectrum. Any absorption bands would necessarily be broad due to the largely amorphous nature of the material (O'Reilly and Mosher 1983, Robertson and O'Reilly 1987).

Diamond is widespread in carbonaceous chondrites with abundances decreasing with increasing metamorphic grade (Ming and Anders 1988, Bernatowicz et al. 1989, Huss 1990). Some of this “diamond” may be partially amorphous or disordered and contain variable amounts of nitrogen, oxygen, and hydrogen (up to 40 atom%) (Blake et al. 1988, Bernatowicz et al. 1989). Diamond, along with graphite, is the main carbonaceous phase in ureilites (Lipschutz 1964, Vdovynin 1970). Meteoritic diamond ranges in size up to ~1 μm (Vdovynin 1970, 1972, Blake et al. 1988). XRD analysis of the diamond sample DIA101 reveals no detectable impurities.

Single crystal diamond transmission spectra indicate that absorption decreases gradually over the range 0.3 to 1.2 μm with the appearance of various absorption bands in the visible region in colored specimens (Davies 1977, Orlov 1977, Woods and Collins 1986, Lilante et al. 1990). Absorption increases slightly over the range 1.5 to 2.6 μm.
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(Sutherland and Willis 1945, Orlov 1977). The reflectance spectrum of the powdered diamond sample (DIA101, Fig. 1) is consistent with these results: reflectance increases sharply in the visible, peaks near 1.2 μm, and declines toward longer wavelengths. The DIA101 sample is colorless, consequently no absorption bands appear in the visible region. Its spectrum is a function of its crystal structure: a large band gap (~ 5.4 eV) semiconductor (Meyerson and Smith 1980) and it differs significantly from the spectra of the other carbon polymorphs.

Carbides

Silicon carbide (SiC) is widespread in carbonaceous chondrites and its abundance declines with increasing metamorphic grade (Bernatowicz et al. 1987, Ming and Anders 1988, Huss 1990). The cosmochemical importance of this phase is discussed below; however, isotopic anomalies seem to be related, at least in part, to SiC grain sizes and perhaps degree of structural order (Anders 1988, Ming and Anders 1988, Zinner et al. 1989, Ash et al. 1990).

The visible and near infrared spectral properties of silicon carbide have apparently not been measured previously. Two grain sizes of silicon carbide, from different sources (SIC101, <37-μm grain size; SIC102, <7-μm grain size), have been spectrally characterized in order to determine the effect of grain size variations on spectral properties (Fig. 2). Both spectra are similar in shape with the finer grain size exhibiting higher overall reflectance. The wavelength position of the reflectance maximum is located at ~0.51 μm in SIC102 and at ~0.42 μm in SIC101. Silicon carbide can occur in a large number of polymorphs (Thibault 1944, Adamsky and Merz 1959, Hannam and Shaffer 1969). XRD analysis of the two samples indicates that they are structurally similar but that the finer grain size sample exhibits a higher degree of disorder. This probably accounts for the SIC102 spectrum exhibiting a broader reflectance maximum and a more gradual reflectance decrease toward longer wavelengths. The cause of the 0.95-μm absorption feature, most evident in the SIC102 spectrum, is unknown. The SiC spectra are distinctly different from the other carbonaceous phases but the overall shape most resembles that of diamond (Fig. 1), suggesting that this material may also be a large band gap semiconductor.

Cohenite ([Fe₆,Ni]₈C) is most abundant in iron meteorites and enstatite chondrites (Brett 1967, Scott 1971). Cohenite and haxonite (Fe₅₄C) are found only infrequently and sparsely in metal grains in carbonaceous chondrites and ureilites (Goodrich and Berkley 1986, Scott and Jones 1990).

The reflectance spectrum of synthetic cementite (Fe₃C) (Fig. 2) is red sloped and featureless, similar to meteoritic metal powders (Johnson and Fanale 1973, Cloutis et al. 1990), indicating that the material retains its metallic character with extensively delocalized electrons. Cementite is spectrally distinct from the other carbonaceous phases, but visible and near infrared spectroscopy is not suited for distinguishing it from metal.

Macromolecular Carbon-Bearing Phases

The bulk of the carbon in carbonaceous chondrites (70 to >95%) is present in a form which is not solvent extractable (Vinogradov and Vdovikin 1964, Hayes 1967, Baker 1971, Nagy 1975, Cronin et al. 1982) and this has hampered efforts to characterize it (Kitajima and Masuda 1992). This material is carbon rich, containing a large amount of high molecular weight multiple ring heterocyclic aromatic components with extensive short aliphatic bridges and side chains (Hayatsu et al. 1977, Hayatsu and
large number of organic phases present in coal precludes the appearance of distinct absorption bands in the ultraviolet and visible regions (Gilbert 1960, Zerla et al. 1990).

The reflectance spectrum of the coal sample (Fig. 3, COAL01) is red sloped as expected. The increase in slope toward longer wavelengths resembles the oil sand spectrum but the lack of absorption bands resembles the oil shale spectrum. The lack of C–H absorption bands is consistent with its low H/C ratio (~0.8) (Tibbetts 1976, Hunt 1979). XRD analysis of the sample indicates that the carbonaceous phase is composed largely of poorly ordered aromatic molecules; kaolinite and illite type clays are the predominant mineral species present.

The coal tar extract sample is coal tar with solvent extractable fractions removed (Gradie and Veverka 1980). Its reflectance spectrum (Fig. 3, CTE101) is relatively dark and flat (<3% reflectance variation) with an absorption feature centered near 0.4 μm. XRD analysis indicates that this material is highly disordered with a broad weak peak near 3.6 Å and extensive low angle scattering. This suggests that the 0.4 μm feature is attributable to electronic transitions in the aromatic molecules present in the sample (Tschanmler and de Ruiter 1963, Ito et al. 1988). The low overall reflectance is also characteristic of a highly disordered material (O’Reilly and Mosher 1983, Robertson and O’Reilly 1987). The reflectance spectrum is similar to coal tar extract spectra measured by other investigators (Gradie and Veverka 1980, Bell et al. 1985, Cruikshank 1987).

Oil sand spectra have previously been measured by a number of investigators (Cloutis 1989, Dougan 1989, Cloutis 1990, Shaw and Kratochvil 1990). The oil sand spectrum (Fig. 3, TAR17) exhibits features attributable exclusively to the organic phase; the solid phase is 95% quartz, which is spectrally featureless (Hunt and Salisbury 1970). The organic phase results in a very red-sloped spectrum and intense C–H absorption bands in the 1.7 μm and 2.3–2.6 μm regions. This is consistent with the high H/C ratio (~1.52) and abundant high molecular weight polyaromatic molecules (Boyd and Montgomery 1962, Yen 1973, Bichard 1987).

The oil shale spectrum also exhibits a red slope but C–H bands are weak or nonexistent (Fig. 3, OILS10). XRD analysis of the sample indicates that the major crystalline phase is quartz with lesser amounts of chlorite and illite. The red slope of this sample is attributable to organic electronic absorptions. Oil shale spectra can exhibit absorption features attributable to the various phases composing the samples (McAskill 1987). The average H/C ratio of the oil shale is ~1.48 (Anders and Robinson 1971) but the structure of the carbonaceous phase differs significantly from that found in the oil sand, consisting largely of aliphatic hydrocarbons (Tissot and Welte 1978). This

FIG. 3. Absolute reflectance spectra of powdered samples of macromolecular organic-bearing materials: coal (COAL01), coal tar extract (CTE101), oil shale (OILS10), and oil sand (TAR17). Vertical scale varies for each sample.


The reflectance spectra of a number of carbon-bearing geological materials with similar characteristics (coal, coal tar extract, oil sand, oil shale) are shown in Fig. 3. They exhibit variations in spectral properties due to compositional differences.

general lack of aromatic hydrocarbons probably accounts for the spectral differences between the oil shale and oil sand. The major mineral species in the oil shale is quartz. Small amounts of plagioclase feldspar, chlorite, and illite/muscovite are also present. None of these phases are apparent in the reflectance spectrum.

DISCUSSION

Reflectance spectra of carbonaceous phases vary significantly among and within the carbon polymorph, carbide, and macromolecular organic-bearing groups. The spectral signatures of the various materials can be attributed to the compositional, structural, and crystallographic properties. The carbon polymorph and macromolecular organic-bearing sample spectra, with the exception of the diamond, are characterized by a broad absorption feature in the ultraviolet–visible region and red-sloped spectra. The absorption feature is attributable to molecular orbital transitions and/or delocalization of electrons located in aromatic structures (Tschemlter and de Ruiter 1963, Silverstein and Bassler 1967, Painter et al. 1981, Fysh et al. 1985, Donini and Michaelian 1986, Ito et al. 1988) although contributions due to photon absorption by stable free radicals, mobile electrons, and charge transfer complexes may also be important (Tschemlter and de Ruiter 1963 and references therein, Ito et al. 1988). The broadness and shape of this absorption feature is a function of the compositional complexity and crystallinity of the material (O'Reilly and Mosher 1983, Robertson and O'Reilly 1987); simple organic compounds do not exhibit red-sloped spectra (Holman and Edmondson 1956, Goddu 1957, Silverstein and Bassler 1967). The wavelength position of the absorption feature can be related to the average size of the aromatic molecules (Sutherland et al. 1944, Badger 1957).

Studies of organic materials, particularly coals, indicate that as the degree of aromatization (also referred to as coalification, carbonization, rank, or C/H ratio) increases, the ultraviolet–visible absorption feature becomes broader and more intense, particularly when carbon content exceeds ~91% (van Vucht et al. 1955, Friedel and Queiser 1956, Tschemlter and de Ruiter 1963, Friedel et al. 1967, McCartney and Ergun 1967, Forrest et al. 1984, Donini and Michaelian 1986, Ito et al. 1988). These spectral and compositional changes also accompany increases in temperature of formation, heat treatment temperature, or degree of metamorphism (Kmetko 1951, Gavrilo and Ernolenco 1975, Rowan et al. 1991), which cause a loss of aliphatics, growth of aromatic complexes (ring condensation), loss of hydrogen, and decrease in the electronic energy gap (Gilbert 1960, Robertson and O'Reilly 1987, Moroz et al. 1991). This results in the wavelength position of the reflectance rise moving toward progressively longer wavelengths (Kmetko 1951, Friedel 1966, Friel et al. 1982).

The samples containing complex mixtures of various hydrocarbons and significant amounts of hydrogen (H/C < 0.2; i.e., coal, oil sand, oil shale) are more red sloped than the carbon-rich materials such as the coal tar extract, graphite, and amorphous carbon. The differences between the maximum and minimum reflectance for any one sample ranges from 12 to 31% in the former group and is <7% in the latter group. The shape of the ultraviolet–visible absorption feature has not been quantified but comparison of the two graphite spectra indicates that the band is broader in the less ordered sample (GRPI02). An essentially amorphous material such as carbon black will exhibit low overall reflectance and an essentially flat or slightly blue slop because the lack of short and medium range order precludes the existence of well-defined electronic energy gaps (O'Reilly and Mosher 1983, Robertson and O'Reilly 1987). Average reflectance in the visible region increases as the degree of order increases (carbon black="amorphous" graphite=natural graphite). The spectral differences between the two SiC samples and between the two graphite samples are attributable to differences in the relative degrees of crystallinity. This indicates that reflectance spectroscopy may be useful not only for identifying carbonaceous phases but also for assessing relative degrees of crystallinity of otherwise compositionally similar materials.

Comparison of the diamond, graphite, and carbon black spectra indicates that the electronic configuration of the carbon atoms will strongly affect the reflectance spectra. A largely amorphous structure results in a dark and relatively featureless reflectance spectrum (carbon black). If the material is more ordered, with carbon atoms in a hexagonal configuration, the reflectance spectrum will assume the characteristics expected for a semimetal with an absorption feature in the low wavelength visible region and a red-sloped spectrum (graphite). If the carbon atoms assume a tetragonal configuration, the reflectance spectrum will assume the characteristics of a large band gap semiconductor (diamond). Each material is spectrally unique (Fig. 1), permitting rapid spectral discrimination of these carbon polymorphs.

POSSIBLE APPLICATIONS

As mentioned, the bulk of the carbon in carbonaceous chondrites is present as a macromolecular insoluble material, which hampers efforts to characterize it (Kitajima and Masuda 1992). The limited analyses available for this material indicate that it consists of a condensed aromatic network with short aliphatic bridges or side chains and substantial atomic substitutions (Hayes 1967, Simmonds et al. 1969, Baker 1971, Bandurski and Nagy 1976, Hay-
TABLE I
Total Carbon Abundances in Various Meteorite Classes

<table>
<thead>
<tr>
<th>Meteorite group</th>
<th>Total carbon (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonaceous chondrites</td>
<td></td>
</tr>
<tr>
<td>CI</td>
<td>2.2–4.8</td>
</tr>
<tr>
<td>CM2</td>
<td>0.9–5.2</td>
</tr>
<tr>
<td>CR2</td>
<td>0.7–3.3</td>
</tr>
<tr>
<td>CV2</td>
<td>0.5–2.0</td>
</tr>
<tr>
<td>CV3</td>
<td>0.1–1.2</td>
</tr>
<tr>
<td>CV4</td>
<td>&lt;0.1–0.2</td>
</tr>
<tr>
<td>CV5/6</td>
<td>0.1–0.3</td>
</tr>
<tr>
<td>CO3</td>
<td>0.1–1.0</td>
</tr>
<tr>
<td>CO4</td>
<td>&lt;0.1–0.1</td>
</tr>
<tr>
<td>Adelaide</td>
<td>0.8</td>
</tr>
<tr>
<td>Ureilites</td>
<td>1.5–5.6</td>
</tr>
<tr>
<td>Ordinary chondrites</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>&lt;0.1–0.4</td>
</tr>
<tr>
<td>L</td>
<td>&lt;0.1–0.9</td>
</tr>
<tr>
<td>LL</td>
<td>&lt;0.1–0.6</td>
</tr>
<tr>
<td>E</td>
<td>&lt;0.1–0.5</td>
</tr>
</tbody>
</table>


atsu and Anders 1981, Zenobi et al. 1989, Murae et al. 1990). This material resembles terrestrial coal, oil shale, or kerogen in some respects but not in others (Schulz and Elofson 1965, Bitz and Nagy 1966, Nagy 1975, Bandurski and Nagy 1976, Cronin et al. 1982, Hayatsu et al. 1983, Wright et al. 1990). Comparisons of the meteorite material with terrestrial carbonaceous materials are complicated by the compositional and structural variations of the former, which are a function of petrologic grade and meteorite class (Cronin et al. 1982, 1988, Hahn et al. 1988, Wright et al. 1990) (Table I). The fact that different organic-bearing geological materials exhibit spectral differences attributable to differences in the composition and structure of the organic phase suggests that visible and near infrared reflectance spectroscopy could fruitfully be applied to characterizing the insoluble organic material in meteorites, a capability that has been demonstrated using infrared spectroscopy (Blob et al. 1988, Murae et al. 1990, Murae 1992).

If the insoluble macromolecular material strongly affects carbonaceous chondrite reflectance spectra, the meteorite spectral slopes should most closely resemble the spectra of solvent insoluble materials such as graphite, carbon black, oil shale, and coal tar extract rather than coal, or oil sand. The available carbonaceous chondrite reflectance spectra have shapes ranging from slightly blue to red sloped, although none are nearly as red sloped as the coal and oil sand spectra (Johnson and Fanale 1973, Salisbury et al. 1975, Gaffey 1976, Gaffey and McCord 1979, Larson et al. 1979, Wagner et al. 1987, Moroz and Pieters 1991). This indicates that the macromolecular phase in carbonaceous chondrites is spectrally similar to terrestrial solvent insoluble phases with carbon in hexagonal arrangements and that the latter may be useful for studying the spectrum altering effects of the former.

Of the various carbon-bearing phases found in meteorites, silicon carbide, diamond, amorphous carbon, and graphite have been singled out because they appear to be carriers of isotopically anomalous elements and primordial noble gases (e.g., Göbel et al. 1978, Bernatowicz et al. 1987, Zinner et al. 1987, Blake et al. 1988, Ming and Anders 1988, Zinner et al. 1989, Amari et al. 1990, Ash et al. 1990, Huss 1990). Most techniques currently used to study these materials involve extensive physical and chemical concentration procedures which may lead to undesirable compositional alterations (Muray 1992). Since these phases are spectrally distinct in the visible–near infrared region, microspectroscopy could be used to (non-destructively) identify, ascertain the degree of order, and map in situ distributions of these and other carbonaceous phases (Blob et al. 1988, Murae et al. 1990, Murae 1992). Microspectroscopy could also potentially be combined with other in situ analytical techniques (Kagi et al. 1991, USRA Quarter 1992, Nittler et al. 1993) to map isotopic anomalies on a grain-by-grain basis and to identify and characterize the carrier in each case.

If the various SiC carriers of isotopic anomalies possess different degrees of crystallinity (Ash et al. 1990), spectroscopy may be useful for distinguishing them on this basis. SiC can also form a large number of polymorphs (polytypes) (Thibault 1944, Adamsky and Merz 1959, Hannam and Schaffer 1969). If these polymorphs are also spectrally distinct (a subject currently under investigation), spectroscopy may prove useful in this area as well, helping to determine whether isotopic anomalies are correlated with SiC structural variations. In situ analyses, relying largely on spectroscopy, should substantially clarify the nature of the various isotopic carriers.

Meteoritic diamonds and diamond-like phases are also carriers of isotopic anomalies and primordial noble gases in carbonaceous chondrites and ureilites (Blake et al. 1988, Ming and Anders 1988, Huss 1990). This material can apparently be somewhat disordered, hydrogenated, or nitrogenated (Vinogradov et al. 1966, Blake et al. 1988, Bernatowicz et al. 1989). Analysis of the diamond phases suffers from their generally low abundances in carbonaceous chondrites (Huss 1990). Given the spectral uniqueness of diamond, it should be possible to use visible–near infrared spectroscopy to identify diamond in situ or in separates.
The substitution of nitrogen for carbon in diamond leads to spectrally detectable changes in infrared absorption bands and wavelength position of the ultraviolet–visible absorption edge (Vinogradov et al. 1966, Orlov 1977). While the crystallographic siting of noncarbon phases in meteoritic diamonds is not known, the results of Orlov (1977) suggest that microspectroscopy may be useful for identifying diamonds which contain spectrally significant amounts of noncarbon elements and for potentially quantifying these amounts.

A large body of meteoritic and observational evidence exists which suggests that B, C, D, F, G, P, and T class asteroids possess abundant opaque (probably carbonaceous) phases on their surfaces (Gaffey et al. 1989). Asteroid reflectance spectra generally become more red sloped with increasing heliocentric distance (Gradié and Tedesco 1982, Hartmann et al. 1987, Cruikshank 1989, Jones et al. 1990, Mueller et al. 1992). The “big picture” scenario of Bell et al. (1989) suggests that the maximum temperature experienced by asteroids decreases with increasing heliocentric distance and decreasing size. The spectral data in conjunction with laboratory and field studies of thermal metamorphism of carbonaceous materials indicate that increasing the temperature of carbonaceous materials results in a number of compositional and structural changes which result in losses of aliphatics and hydrogen and the development of a progressively more ordered aromatic structure (van Vucht et al. 1955, French 1964, Friedel et al. 1967, Sugiuira et al. 1986, Ito et al. 1988, 1990, Moroz et al. 1991, Ikeda 1992). Spectrally this will result in a decrease in overall reflectance, a possible increase in ultraviolet–visible absolute reflectance (Davis 1978), and a decrease in overall spectral slope with the wavelength position of the reflectance rise moving toward progressively longer wavelengths (Kmetko 1951, Friedel 1966, Friel et al. 1982). The increase in spectral slope is seen for the dark asteroid classes with increasing heliocentric distance (Mueller et al. 1992), consistent with the expected spectrum altering effects on carbonaceous phases subjected to a radially decreasing heat source (Bell et al. 1989) and consistent with the current spectral results indicating decreasing spectral slope accompanying progressive increases in temperature. A more comprehensive examination of the origin and evolution of carbonaceous materials on asteroids in light of the available spectral/compositional information for carbonaceous materials is currently in preparation.

The carbonaceous phases in IDPs have yet to be fully characterized (Gibson 1992 and references therein) but the diversity of identified materials suggests that microspectroscopy could be used to identify and map the distributions of carbon phases in these particles and assist in identifying the carriers of isotopic anomalies (McKeegan et al. 1985, Gibson 1992).

The increasing order and associated structural and compositional changes accompanying thermal metamorphism are usually amenable to X-ray diffraction analysis (Mueller 1953, Rietmeijer and Mackinnon 1985a). If a correlation between diagnostic spectral parameters and the X-ray diffraction data can be established it will open up the possibility of using spectroscopic techniques to conduct remote spectroscopic geothermometry on asteroids.

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REFERENCES


CLOUTIS, GAFFEY, AND MOSLOW


Cloutis, E. A. 1996. Identification, detection and characterization of individual tar sand phases using diffuse reflectance spectroscopy (0.35–2.6 μm). AOSTRA J. Res. 6, 17–27.


Griffin, G. M. 1967. X-ray diffraction techniques applicable to studies of diagenesis and low rank metamorphism in humic sediments. J. Sedim. Petrol. 37, 1006–1011.


Lochmuller, C. H., R. Rohl, and D. B. Marshall 1981. Use of...


SPECTROSCOPY OF CARBONACEOUS MATERIALS


Scott, E. R. D., and R. H. Jones 1990. Disentangling nebular and asteroidal features of CO\textsubscript{3} carbonaceous chondrite meteorites. Geo-


Simmons, P. G., A. J. Bauman, E. M. Bollin, E. Gelpi, and J. Oró 1969. The unextractable organic fraction of the Pueblito de Al-


