The Composition of Planetesimal 5145 Pholus

NASA-TM-112311

D. P. Cruikshank[1]   NASA Ames Research Center, MS 245-6, Moffett Field, CA, 94035 [Phone 415-604-4244] e-mail CRUIKSHANK@SSA1.ARC.NASA.GOV

T. L. Roush   San Francisco State University and NASA Ames Research Center

M. J. Bartholomew   Sterling Software and NASA Ames Research Center

L. V. Moroz   Vernadsky Institute, Russian Academy of Sciences, Moscow, Russia, 117975

T. R. Geballe   Joint Astronomy Centre, 660 N. Aohoku Pl., University Park, Hilo, HI, 96720

S. M. White   NASA Ames Research Center

J. F. Bell, III   Cornell University, Ithaca, NY 14853

Y. J. Pendleton   NASA Ames Research Center

J. K. Davies   Joint Astronomy Centre, 660 N. Aohoku Pl., University Park, Hilo, HI, 96720

T. C. Owen[1]   Institute for Astronomy, 2680 Woodlawn Dr., Honolulu, HI, 96822

C. deBergh[1]   Observatoire de Paris, Paris, France

D. J. Tholen[1]   Institute for Astronomy, 2680 Woodlawn Dr., Honolulu, HI, 96822

M. P. Bernstein   NASA Ames Research Center

R. H. Brown   Jet Propulsion Laboratory

K. A. Tryka   Dept. of Physics, Northern Arizona University, Flagstaff, AZ

[1] Guest observer at the United Kingdom Infared Telescope (UKIRT). UKIRT is operated by the Joint Astronomy Centre on behalf of the United Kingdom Particle Physics and Astronomy Council.

Submitted to **Icarus**, April 25, 1996

ABSTRACT

We present a new spectrum of 5145 Pholus between 1.15 and 2.4 μm. We model this, and the previously published (0.4-1.0 μm) spectrum, using Hapke scattering theory. The 2.04 μm band of H_2O ice is seen in absorption, as well as a strong band at 2.27 μm, interpreted as frozen methanol and/or the methanol photo product hexamethylenetetramine (HMT). The presence of small molecules is indicative of a chemically primitive surface, since heating removes the light hydrocarbons in favor of macromolecular carbon typically found in carbonaceous meteorites. The unusually red slope of Pholus' spectrum is matched by fine grains of Titan tholin, as found previously by Hoffmann et al. [**J. Geophys. Res. 98**, 7403-7407, 1993] and Wilson et al. [**Icarus 107**, 288-303, 1994]. Object 1993 HA2, which has an orbit similar to that of 5145 Pholus, is similarly red, but there are as yet no observations of absorption bands in its spectrum. We present a model for the composite spectrum of all spectroscopic and photometric data available for 5145 Pholus and conclude that this is a primitive object which has yet to be substantially processed by solar heat.

INTRODUCTION

On 9 January 1992, the Spacewatch asteroid search project discovered object 1992 AD, now designated 5145 Pholus, in a highly eccentric orbit that passes from a perihelion point just inside the orbit of Saturn to well outside the orbit of Neptune at aphelion, with a period of 92.7 years (Scotti 1992, Marsden 1992). Measurements of the thermal flux (Howell 1992) indicate that the diameter of Pholus is at least 140 km and the albedo is <0.08 at 0.55 μm. Similar thermal flux measurements (Davies et al. 1993a) suggest a minimum diameter of about 190 km and albedo (at 0.55 μm) of 0.04. Photometric observations (Buie and Bus 1992, Hoffmann et al. 1993) yield a rotation period of 9.98-9.99 hours, and suggest that the object is irregular in shape.

While the orbit of Pholus is comet-like, its dimensions are an order of magnitude greater than those of a typical comet nucleus and are more similar to many asteroids. Pholus does not clearly fall into either classification. Indeed, both classifications have become rather indistinct in recent years, with the realization from orbital dynamics that some objects long considered asteroids are inactive comets (e.g., Hartmann et al. 1986), and the detection of cometary activity in some objects designated asteroids (Meech and Belton 1990). Further, recent discoveries of small bodies beyond the orbit of Pluto (Jewitt and Luu 1995) challenge the traditional definitions of both comets and asteroids. For the purpose of this paper, we refer to Pholus as a planetesimal, that is, a body which condensed in the solar nebula at the time of planet formation, and which has subsequently undergone minimal physical and chemical processing. At the time of this writing, no spectroscopic or direct imaging evidence for cometary activity has been detected on Pholus.

Photometric and spectrophotometric observations made shortly after the discovery showed that Pholus was the reddest object in the solar system measured to that time (Mueller et al. 1992, Fink et al. 1992, and Binzel 1993). In this context, "red" means that with the color of the Sun removed, the spectral reflectance of the body increases toward longer wavelengths over the interval 0.3 - 1 μm. Each of the three observing groups referenced above independently proposed that the surface of the object is covered, at least in part, by organic solids which impart the extraordinary red color and low reflectance at wavelength 0.55 μm. Refractory organic solids produced in experiments in which energy is deposited in gases and in ices exhibit a red color similar to that of Pholus. However, it is difficult to establish an identification of a specific substance on the basis of the reddening characteristic alone.

Apart from methane, specific organic molecules in the solid state have been identified by remote sensing observations of Solar System objects. This is partly because it is only possible to

3

observe a small portion of the infrared spectrum where diagnostic absorptions occur. This situation is further complicated by the vast number of possible molecular combinations of even a small number of carbon and hydrogen atoms. One can, however, search for evidence of functional groups, such as methyl (CH_3) and methylene (CH_2), as revealed by the frequencies of the stretching and deformations of their chemical bonds. But the fundamentals of these bonds occur in the infrared at >3 μm, while our observational window for faint Solar System bodies is currently constrained (by technology) to ≤2.5 μm. We must therefore search for molecular identifications through relatively weak overtone bands (of the fundamental frequencies) as well as combinations of stretching, bending, scissoring frequencies of the various chemical bonds that hold a given molecule together. Within the framework of this poorly constrained problem, ambiguous and non-unique identifications are to be expected.

An infrared spectrum (1.4-2.4 μm) of 5145 Pholus obtained by Davies et al. (1993b) in 1992 showed a strong absorption band centered near 2.27 μm, absorption at 2.0 μm, and other less distinct structure at shorter wavelengths. Davies et al. (1993b) noted a resemblance to an absorption band in the tholins described by Sagan and Khare (1979) and for which reflectance spectra are shown in Cruikshank et al. (1991), however a firm identification of this organic solid could not be made. Wilson et al. (1994) explored the comparison with tholins more thoroughly and on the basis of reflectance spectra proposed mixtures of a specific tholin, HCN polymer, and H_2O and NH_3 ices. We return to this work below. Cruikshank et al. (1993a) noted the similarity in the position and shape of the 2.27 μm Pholus band to that in terrestrial organic solids which are rich in light soluble hydrocarbons (bitumen). The authors proposed that Pholus' surface contains small hydrocarbon molecules indicating a more chemically primitive surface than exhibited by the D and C-type asteroids and comets. Luu et al. (1994) also observed the 2.27 μm Pholus band and noted the similarity to, but particularly the difference from the bitumen band in terrestrial tar sand.

Two of the three observational data sets for the photovisual spectral region (Fink et al. 1992; Binzel 1993) are in good agreement, with relatively minor differences in the steep red slope that each shows. The spectral reflectance derived by Mueller et al. 1992, however, is less steeply sloped toward the red. While some of these differences may result from the different solar phase angles at the time of the observations (Wilson et al. 1994), systematic errors in the flux calibration, induced by the standard stars used, may also contribute. For present purposes we regard the spectral region 0.3-1.0 μm sufficiently well determined and do not offer any new observations.

ANALYSIS OF THE INFRARED SPECTRUM

Our first task has been to obtain improved spectral data of Pholus in the near-infrared (1.2-2.5 μm) in order to provide the basis for a more specific identification of solids on the surface. Because Pholus is very faint, we have been able to obtain only parts of the spectrum during several observing sessions. In this paper we present a composite spectrum derived from our own observations and those of Luu et al. (1994).

The improved spectral data (1.15-2.4 μm) reported here were obtained on several occasions in 1993-1995, with the United Kingdom Infrared Telescope and the Cooled Grating Spectrometer-4 (CGS4) (Table I).

CGS4 is a cryogenic spectrometer using a diffraction grating and a two-dimensional InSb array detector. We normally used the system in the low-resolution mode (first order of the 75 lines/mm grating, 150 mm focal length camera), which at 1.6 μm gave resolution R = $\qquad$ = 250, and at 2.2 μm R = 340. Until early 1995, CGS4 used a 58 X 62 pixel detector array; with the grating and camera configuration noted, a single setting of the grating gave a spectral interval of 0.405 μm on the array. Some of the

data, particularly those in the 1.2 μm region, were taken with the grating in the second order, giving R = 383 at 1.2 μm and spectral coverage of 0.202 μm with a single setting. The data obtained in 1995 were taken with a new InSb detector array of 256 X 256 pixels, giving 0.66 μm spectral coverage with a single setting of the grating in the first order. At 2.2 μm with the new array, the resolution is R = 850.

The wavelength calibration for CGS4 is determined from spectral lines produced by Ar and Kr lamps within the spectrometer each time the position of the grating is changed. The absolute wavelength calibration has been checked against the OH emission lines in the night sky, and the rms accuracies from quadratic fits to several lines in each spectral interval are typically 0.0001 μm. Stars of near-solar spectral type and known flux are observed at the same or comparable airmass as the target objects, with no change in the grating position. Division of the spectrum of Pholus by the stellar standard removes the effects of telluric lines and establishes the spectral flux distribution of the target object. This procedure is subject to limitations of seeing conditions and other systematic effects, such as the stability of the local water vapor content of the atmosphere, which affects the ability to remove strong telluric absorption lines.

Uncertainties in the absolute flux of Pholus were primarly caused by inferior seeing conditions when the image of Pholus did not entirely fall within the slit of the spectrometer. Broadband photometric measurements (at VJHK wavelengths; see Table II) were used to join the various components of the spectrum observed over the four year period. For reasons discussed below, we have prepared two versions of a composite spectrum, using our own new data, those of Davies et al. (1993b) and Luu et al. (1994), weighted according to the signal/noise in each component. JHK photometry was obtained by Davies and Sykes (1992), Davies et al. (1993b), and Howell (1995). The photometric measurements by Howell (1995) were especially important in linking the near-

6

infrared spectra reported here to the visible-region brightness of Pholus because she obtained JHK measurements with one telescope while V measurements were being made simultaneously with another telescope at the same observatory site. This simultaneity of the VJHK measurements obviates the problems of corrections for phase angle and, especially, the brightness variation of Pholus as it rotates. We note that Davies and Sykes (1992) and Davies et al. (1993b) used estimated values of V for the times of their JHK observations for the calculation of the V-J color. Their V-J is not substantially different from that observed directly by Howell (1995), and we therefore average the two determinations by Davies and Tholen (1996) with the Howell value to obtain V-J = 2.50 ± 0.08, and the other colors, as given in Table II. In calculating this average we make no corrections for phase angle because we have no direct and reliable information on phase-color effects for an object with the highly unusual colors of Pholus.

In order to derive the reflectance spectrum relative to 0.55 μm, the colors of the Sun were subtracted from the average V-J, V-H, and V-K colors of Pholus. The solar colors used were those of Campins et al. (1985): V-J = 1.12, V-H = 1.43, V-K = 1.49. The resulting intrinsic colors of Pholus at the J, H, and K wavelengths were then converted to reflectances relative to V, for which we assumed p_V=0.06, a value consistent with the radiometric determinations mentioned above.

THE COMPOSITE SPECTRUM

We elected to compile two versions of the composite spectrum because certain data sets show evidence, albeit at the margin of certainty, of absorptions bands that do not appear in other sets. These include the absorption centered near 1.71 μm suggested in the Luu et al. (1994) spectrum and in that of Davies et al. (1993b); in other data sets it is not even marginally seen. Furthermore, as noted below, the Luu et al. spectrum shows marginal evidence for a band at 2.33 μm. Finally, a spectrum by

Davies and Tholen from 1.15-1.83 μm (see Table I) depicts an
upward curvature at 1.4-1.5 μm that is more consistent with the
H_2O ice band in our model than the shape of the spectrum in other
data sets. Therefore, in order to preserve the possibility that
as the body rotates different hemispheres of Pholus have
different spectral signatures, we present two versions of the
composite spectrum.

The first version of the composite spectrum (Fig. 1) consists of
a weighted average of all the data in Table I except the
spectrum of 19 April 1994 by Davies and Tholen. In spectral
regions of overlap between our data set and that of Luu et al.
(1994), all of our spectra were resampled at the same wavelengths
as Luu et al. so that averages could be computed. All spectra
were taken with the same spectrometer and telescope. The version
shown in Fig. 1a includes no data in the J wavelength region.
Large symbols in Fig. 1a represent the JHK photometry in Table II.

The second version of the composite spectrum (Fig. 2a) was
prepared as that in Fig. 1a, except that the region 1.15-1.83
consists of a spectrum obtained on a single night (19 April 1995)
by Davies and Tholen.

In both Figs. 1a and 2a, the region from 1.87 to 2.4 μm shows
distinct spectral features, notably the broad band between 1.9
and 2.2 μm and the sharp band centered at 2.27 μm. Telluric
water vapor and CO_2 absorb between 1.87 and 2.1 μm, making this
region difficult to observe, but particularly dry atmospheric
conditions and careful attention to standard star observations
made it possible to determine Pholus' spectrum through this
region with full correction for the telluric absorptions.

THE MODEL

We modeled the spectrum of Pholus using the Hapke theory for
diffuse reflectance from an airless planetary surface (Hapke
1993). The formulation we used has been described by Roush et

8

al. (1990) and Roush (1994); in the present context we used models of intimate compositional mixes of grains and spatially segregated regions of differing composition, as described below. Calculations using the Hapke theory require the real and imaginary indices of refraction for the candidate materials to be specified, but such information is available for only a limited number of plausible components of the surface of Pholus. The limited availability of appropriate optical constants somewhat constrained our range of model computations, but we began on the assumption that specific regions of the spectrum would be most affected by specific constituents, and that a final model would have to incorporate all of the components that are chemically plausible.

We begin by matching the red slope of the spectrum from 0.4 to 1.0 um, using the optical constants published by Khare et al. (1984a) for Titan tholin. We have elected to fit the photovisual region data of Binzel and Fink et al., which are in good mutual agreement, rather than the data of Mueller et al., which has a somewhat less-red slope. The material called Titan tholin is made by plasma irradiation of a gas mixture of $N_2+CH_4 = 0.9+0.1$, corresponding approximately to the bulk composition of Titan's lower atmosphere (Khare et al. 1984b). Titan tholin consists of a variety of C_1-C_5 hydrocarbons and nitriles, both unsaturated and saturated (Thompson et al. 1991), the most abundant of which have been observed in Titan's stratosphere by the Voyager infrared spectrometer (Hanel et al. 1981). Other compounds in Titan tholin include alkanes, alkenes, and nitrogen heterocyclic molecules (Khare et al. 1984b; Ehrenfreund et al. 1994). Upon acid hydrolysis of Titan tholin, some 16 amino acids are produced, with glycine the most abundant (Khare et al. 1986). Recent spectroscopic and chromatographic analysis of Titan tholin (McDonald et al. 1994) confirms earlier work demonstrating that aromatic hydrocarbons are a minor component. The water-soluble fraction of this tholin is dominated by materials of molecular weight ~200-600 amu. McDonald et al. (1994) quantified the production of amino acids from Titan tholin, confirming the

9

dominance of glycine, and provided other compositional details. Overall, the elemental composition of Titan tholin is represented by $C_3H_5N_2$ (Sagan et al. 1984).

Qualitative inspection of the spectrum of Pholus by the authors referenced above suggested that this tholin might match the red slope satisfactorily, and Wilson et al. (1994) demonstrated through their own Hapke scattering calculations that such is indeed the case. Because our primary focus in this work has been to model the spectral absorption features in the near-infrared, we have concentrated our efforts on other materials because neither tholins nor the other materials included in the Wilson et al. preferred models match the band positions, band shapes, or the albedo levels (>1.8 μm) in the new spectral data.

The broad absorption band centered near 2.04 μm is well matched by absorption in solid H_2O. This band is seen in comparable strength in comet 1995 O1 (Hale-Bopp) (Davies et al. 1995, 1996) and in Saturn's satellite Phoebe (Owen et al. 1996); both of these bodies have low visual albedo. Optical constants for low-temperature H_2O ice derived from measurements by Ockman (1957) (Roush 1996) were used in our calculations. The Pholus absorption band at 2.27 μm is matched in position and qualitatively in shape by a band in solid methanol (CH_3OH) (Sandford and Allamandola 1993). Because CH_3OH in a vapor state has been detected in several comets (Hoban et al. 1991, Bockelée-Morvan et al. 1991, and the review by Mumma et al. 1993), the solid phase is a plausible component of Pholus. Optical constants for solid CH_3OH at wavelengths shorter than 2.5 μm are not available in the literature, so we undertook to determine them from new laboratory spectra obtained by us in the laboratory of Dr. Vincent Anicich at the Jet Propulsion Lab. The transmission spectrum of a frozen film of 13.67 μm thickness was obtained at 90 K, and the real and imaginary indices of refraction were calculated (see Appendix B). Fig. 3 gives an overview of the solid CH_3OH spectrum.

The spectrum from which we calculated the indices for CH_3OH is in good agreement with that shown by Sandford and Allamandola (1993). In addition to the distinct band at 2.27 μm, there is a weaker band at 2.33 μm, and an OH absorption centered at 2.1 μm. We return later to the assignments of these bands.

The three components discussed so far have high albedos when seen in diffuse reflectance, while the surface of Pholus has a very low albedo in visible wavelengths. Therefore, we have introduced into our models a fourth component to lower the albedo to match that of Pholus. We use carbon black, a form of elemental carbon that has very high absorption across the visible and near infrared spectrum, and is quite neutral in color. This component is added as a spatial component by using the laboratory reflectance spectrum measured for carbon lampblack.

Our best fitting model of the Pholus spectrum consists of two principal components. The first is an intimate mixture of 33 percent tholin with grain size 1 μm, 33 percent H_2O ice with grain size 10 μm, and 34 percent CH_3OH ice with grain size 10 μm. Within this intimate mixture of the three grain types, an incident photon encounters all three kinds of grains before leaving the surface. The second principal component is carbon black. The two components are modeled together as a spatially segregated mixture; a photon scattering from one component does not strike the other before leaving the surface. The best-fitting mixture of the two principal components required to achieve the albedo of Pholus at every wavelength is 63 ($\pm$5) percent carbon black and 37 ($\pm$5) percent of the tholin-ice-methanol mixture.

We found that in order to achieve the steep red slope at the correct albedo level in the visual spectral region, tholin grains of 1 μm were required. This small size violates the principle adopted for Hapke scattering models that the grain size must be at least three times the wavelength (in the same units). There are several ways to increase the particle sizes we use. One is

to scale the optical constants of the tholin to retain the visual slope but to be less absorbing. This would likely result in larger abundances of tholin contained in the mixtures. Another approach would be to increase the internal scattering within particles; this would have the net effect of increasing the grain diameters for all components. Instead of taking either of these ad hoc approaches, we simply note that the tholin grain size violates assumptions associated with Hapke theory.

METHANOL

Our model incorporates CH_3OH to account for the 2.27 μm band, but methanol also has a second sharp band a 2.33 μm which does not appear in the composite Pholus spectrum. This pair of bands arises as combinations of the CH stretching and deformation modes. The many modes of CH_3OH have been identified by Barnes and Hallam (1970) for monomers, dimers, and multimers in an Ar matrix. The asymmetric stretching fundamentals lie at 3005.3 (as1 [our notation]), 2961.9 (as2), and 2956.0 (as3) cm^{-1}, with the symmetric stretch at 2847.9 cm^{-1} (ss1). The asymmetric deformation fundamentals lie at 1474.1 (ad1) and 1465.8 (ad2) cm^{-1}, and the (weak) symmetric deformation at 1451.4 cm^{-1} (sd1). The 2.27 μm (4405 cm^{-1}) band in our model is the combination of the asymmetric stretching and deformation (as2+ad1, as2+ad2, as3+ad1, as3+ad2), while the 2.33 μm (4292 cm^{-1}) band is the combination of the symmetric modes. The symmetric fundamental modes are characteristically weak, particularly in the deformation mode (sd1), resulting in a significantly weaker combination band. The combinations as1+ad1 and as1+ad2 do not appear in the methanol spectrum.

As an abundant molecule in interstellar space and comets, CH_3OH is an important potential component of the surface of a relatively unprocessed planetesimal such as Pholus. Because CH_3OH is a small molecule and because it is readily produced by the oxidation of CH_4, the presence of methanol is indicative of

12

the chemically primitive nature of a surface rich in hydrocarbons. In addition to CH_3OH, gaseous CH_4 has been found in Comet C/1996 B2 (Hyakutake) (T. C. Owen, private communication).

Does solid CH_3OH exist on the surface of Pholus? In the composite spectra we present here, only the 2.27 μm band of CH_3OH is clearly visible, while the weaker 2.33 μm band is not. However, in the single spectrum of this region published by Luu et al. (1994), which is included in our composite, there is a suggestion of the 2.33 μm band very close to the level of the noise in the data. In Fig. 4 we show the Luu et al. spectrum and our model, which includes CH_3OH ice, for comparison.

While solid CH_3OH may occur on Pholus, in consideration of the absence of the 2.33 μm band in most of the individual spectra and in the composite, we do not claim that we have identified it in this work. We reiterate, however, that methanol is an abundant component (at the level of a few percent relative to H_2O) of at least some active comets, which are probably closely related to Pholus. We carry CH_3OH in our models because it represents small hydrocarbon molecules, such as the photochemical products of methanol discussed in the next section, and because it's optical indices have been measured, which is not the case for other potential materials.

HEXAMETHYLENETETRAMINE

Spectroscopy of the dense interstellar medium (protostars embedded in interstellar gas and dust clouds [e.g., W33A] and stars behind dense molecular clouds [e.g., Elias 16]) shows the presence of ices of H_2O, CO, OCS, CH_3OH, and XCN, plus numerous bands for which the identification is presently uncertain. Ultraviolet photolysis experiments with mixtures of ices that are analogs of the ices found on interstellar grains produce a solid residue that is chemically stable at room temperature and pressure (Allamandola et al. 1988). This residue provides a good

13

spectroscopic match to the 3.4-um region in the spectra of the diffuse interstellar medium where C-H stretching modes dominate (Sandford et al. 1991, Pendleton 1993, 1995; Pendleton et al. 1994). Recent studies of the residue (Bernstein et al. 1995) show that it is composed of ˜60 percent $(CH_2)_6N_4$ (hexamethylenetetramine, or HMT), while the remaining ˜40 percent is a mixture of amides and ketones. HMT is potentially a very important molecule because it carries four atoms of nitrogen and its synthesis incorporates NH_3. Nitrogen and ammonia appear to be underabundant in the interstellar medium (Van Dishoeck et al. 1993) and in comets (Mumma et al. 1993), and thus HMT offers a possible component to account for the deficiency.

HMT is produced by the UV photolysis of mixtures of the ices of $H_2O:CH_3OH:CO:NH3 = 100:50:10:10$, and in other ratios (Bernstein et al. 1994, 1995). Bernstein et al. (1995) favor a synthesis mechanism in which formaldehyde is first formed by UV photolysis of methanol and then reacts with ammonia to form methyleneimine (CH_2NH). This path, plus the subsequent reactions, is shown in Fig. 5 from Bernstein et al. (1995).

We have obtained reflectance spectra of HMT in the region 0.2 to 2.5 μm at room temperature (see Appendix). The near-infrared portion of this spectrum is shown in Fig. 6 along with that of solid methanol and the spectrum of Pholus. HMT has a distinct absorption band at 2.27 μm, just as does solid CH_3OH, but in place of methanol's distinct secondary band at 2.33 μm, HMT shows an absorption shoulder with minor spectral structure extending to about 2.40 μm, which is a better match to the spectrum of Pholus than is solid CH_3OH. We have not yet been able to model the Pholus spectrum using HMT because the optical constants for this material have not yet been determined in the spectral region of our data.

The 2.27 μm band is a combination of the C-H asymmetric stretching and bending modes, but in CH_2 rather than CH_3, as in the case of CH_3OH. Bernstein et al. (1995) studied HMT in H_2O

14

ice, in Ar ice, and as a pure substance. They denote the CH_2 deformation as ν_{19} and the asymmetric CH_2 stretch as ν_{17}. The calculated combinations $\nu_{17} + \nu_{19}$ all occur within an interval of 0.01 μm, with the average at 4417.2 cm^{-1} (2.264 μm). In our spectrum of HMT (diluted in powdered MgO), the central wavelength is 2.27 μm. The symmetric mode ($\nu_{18} + \nu_{19}$) in HMT is weaker, and the coresponding combination band at 4335.1 cm^{-1} (2.307 μm) contributes to the long wavelength wing of the asymmetric combination.

When an ice mixture of H_2O and CH_3OH is bombarded with ions it produces acetone [$(CH_3)_2CO$] (Strazzulla et al. 1995). The reaction procedes no further toward HMT. If NH_3 were to be included in the mixture, the reaction is expected to procede no further than the imine of acetone.

Because the photolysis of CH_3OH results in the production of formaldehyde, HCOH, as an intermediary toward the formation of HMT, and because HCOH is found in comets, we have considered the possibility that HCOH is responsible for the features seen in the spectrum of Pholus. Formaldehyde readily polymerizes to two forms, the trimer (trioxane, $(HCOH)_3$) and the linear polyoxymethelene ($(HCOH)_n$, or POM). POM was found by the Giotto spacecraft in the coma dust of Comet P/Halley (Huebner 1987, Mitchell et al. 1987, but also see Mitchell et al. 1992). We show in Fig. 6 our reflectance spectrum of polyoxymethelene, which shows structure in the 2-2.5 μm region, but which does not match the structure in the spectrum of Pholus.

There are additional molecules related to HMT and the multimer forms of formaldehyde; in Fig. 6 we include a reflectance spectrum of $(CH_2)_3(NH)_2$ piperazine obtained by us. This is a cyclic compound with partial NH substitution for CH_2. Piperazine does not show the 2.27 μm band that we see on Pholus.

We have been unable to determine the refractive indices of HMT and the other solids for which we obtained reflectance spectra,

15

and although HMT provides a better qualitative match to the 2.27 μm region of Pholus' spectrum than solid CH_3OH, we use the refractive indices for CH_3OH in our model.

Returning to the question of the presence of CH_3OH on the surface of Pholus, we note that the Luu et al. (1994) spectrum may show 2.33 μm band in addition to that the stronger 2.27 μm band, although the model shows a recovery in intensity to the level of the local continuum, while that of Pholus does not. As we noted before, the composite spectra we derived do not show both bands, and CH_3OH would appear to be undetected. The composite spectra appear to be more consistent with the spectrum of HMT in this same region, because HMT shows only a band at 2.27 μm and an absorption shoulder at longer wavelengths matching that of Pholus.

HMT decomposes in the presence of heat, UV irradiation, and acid hydrolysis, as shown in Fig. 5, into many cosmochemically interesting materials, including some of the original materials from which it is synthesized. Acid hydrolysis produces amino acids, ammonia, and formaldehyde, all of which are of significance in the Solar System. Bernstein et al. (1995) suggest that photolyzed HMT is the source of the XCN in the dense interstellar medium (Lacy et al. 1984; Tegler et al. 1993, 1995; Pendleton et al. 1996), and possibly the CN seen in comets.

MINERALS

Many minerals show relatively narrow spectral features in the 2.2-2.4 μm region. Reflectance spectra of ten such minerals are given by Bell et al. (1994, Fig. 7), and we have further examined the spectra of nine chlorites and perchlorites in the USGS Digital Spectral Library (Clark et al. 1993). We found no plausible minerals that have the 2.27 μm Pholus band with the correct central wavelength and band shape. Although there may be other minerals not examined by us that have a spectrum similar to that of Pholus in the near-infrared, we do not pursue this

possibility further, and return our focus to volatiles and
hydrocarbons.

THE WILSON ET AL. MODEL

Wilson et al. (1994) used Hapke scattering theory to compute a
synthetic spectrum to match that of Pholus. They used optical
constants of ices and hydrocarbons in various combinations for a
hypothetical material that would match the red color (0.4-1.0
μm). They concentrated their study on the photovisual spectral
region, using the same data presented here (Fink et al. 1992,
Mueller et al. 1992, Binzel 1993). Their study incorporated the
original near-infrared spectrum by Davies et al. (1993b).
Using the real and imaginary refractive indices of a variety of
individual materials, they sought mixtures (termed intraparticle
mixtures) of these materials that, when the individual n and k
values of which were added in a linear way, would reproduce the
hypothetical bulk material matching the spectrum of Pholus.

We note that Wilson et al. used refractive indices of H_2O ice
from Warren (1984), which are for ice at T ˜ 269, whereas in our
models we use indices for ice at the more appropriate
temperature T ˜ 100K. Although the differences in the indices
are slight, there is a small shift to longer wavelengths of the
ice band centers and a narrowing of the bands with decreasing
temperature.

Wilson et al. favored two intraparticle mixtures. One mixture
(HTW) consists of 0.15 Titan tholin, 0.1 hydrogen cyanide
polymer, and 0.75 H_2O ice (particle size 10 μm). The second
model (HTA), giving a better fit to the spectrum, consists of the
same components except that NH_3 ice is substituted for H_2O and a
pure hydrocarbon tholin (having no nitrogen) is substituted for
the Titan tholin.

In Fig. 7 we reproduce the best of the two preferred Wilson et
al. models (HTA) for comparison with our newly derived spectrum

17

in the near-infrared and the three previously published data sets in the photovisual spectral region. For Fig. 7 we have recalculated the model from the Wilson et al. HTA recipe in terms of geometric albedo, whereas Wilson et al. worked with normalized brightness. The discrepancies between the model and the data arise for > 1.4 μm, and are particularly evident in the mismatch between the strong NH_3 absorption bands (2.01 and 2.24 μm) and the broader absorption bands in Pholus' spectrum at nearby but somewhat different central wavelengths.

We believe that the technique of Wilson et al. (1994) for deriving the composition of a planetary surface is flawed by their reasoning that optical constants (n, k) of a real mixture can be drived by the linear addition, on a molar fractional basis, of the refractive indices of real materials to sum up to the indices of a hypothetical molecule. A molecular mixture of two or more materials will have real and complex refractive indices that are not a simple sum of the indices of the individual components. In some cases, as with small amounts of CH_4 dissolved in solid N_2, significant wavelength shifts in the maximum values of the imaginary index of refraction, k, arise (Schmitt and Quirico 1992; see also Cruikshank et al. 1993, Quirico and Schmitt 1996). These shifts would not be predicted in the linear addition of k values for a hypothetical molecular mix. A more physical model under the present circumstances is the intimate mixture, described above and in Cruikshank et al. (1993b) in which photons scattered from a grain of one component also encounter from grains of all the other components before emergence from the surface.

THE HOFFMANN ET AL. MODEL

Hoffmann et al. (1993) calculated Hapke scattering models using Titan tholin (grain size 3 μm) and neutral colored materials of high and low albedo. They found a satisfactory match to the spectrum of Pholus by Fink et al. (1992), 0.4-1.0 μm, but did not consider the near-infrared region. Wilson et al. (1994) discuss

the Hoffmann et al. model in the context of their preferred
mixtures, and we do not consider the Hoffmann work further here,
because our emphasis is on the near-infrared region, and neither
the Titan tholin (alone) nor neutral materials match that portion
of the spectrum.

THE ASPHALTITE MODEL

On the basis of laboratory spectra of a suite of natural
terrestrial organic solids by Cloutis (1989) and Moroz et al.
(1991, 1992), Cruikshank et al. (1993a) proposed that the red
color and the 2.27 μm absorption band of Pholus might be matched
by similar features shown by those materials. The solids studied
were tar sands, asphaltite, kerite, anthraxolite, etc., all
containing varying amount of solvent-soluble hydrocarbons of low
to medium molecular weight (<500 amu), collectively called
bitumen. In his search for diagnostic spectral features for
remote sensing of organic solids on solar system bodies and on
Earth, Cloutis (1989) identified near-infrared absorption bands
in natural tar sands with specific overtones and combinations of
C, H, and O vibrational fundamental modes. Tar sand contains
macromolelcular organic material that is related to petroleum,
coal, and kerogen.

The most familiar macromolecular carbon material is kerogen.
Kerogen is the fraction of organic matter which is insoluble in
the usual organic solvents, and is frequently referenced in
connection with meteorite and asteroid organics (e.g., Cruikshank
and Kerridge 1992, Cronin et al. 1988, Cloutis et al. 1994). In
a terrestrial setting, where organic solids result from thermal
processing of the decay products of biological activity, kerogens
are members of the sequence of natural terrestrial carbonaceous
materials representing a continuous sequence from oil through
coal to graphite. The sequence is distinguished in large part by
the changing ratio H/C; oil has the highest H/C, while graphite
is pure C. Asphaltites (H/C~1-1.6), kerites (H/C~0.6-1.4), and
anthraxolites (H/C~0.03-0.1) are solid non-graphitic members of

19

this sequence, with anthraxolite being essentially the equivalent of kerogen. The degree of aromaticity (predominance of carbon ring structures) increases with decreasing H/C, ultimately terminating in the hexagonally structured graphite, devoid of hydrogen.

Asphaltite, kerite, and tar sand show a strong absorption band centered at 2.285 μm and having a profile similar to that of the 2.27-μm band of Pholus. The mismatch in wavelength is too large to explain in terms of temperature or minor compositional effects. Thus, we abandon for the present time the proposal by Cruikshank et al. (1993a) of a strong compositional similarity.

The comparison of terrestrial organic solids with bodies in space retains considerable value; a coal model of the interstellar extinction by Papoular et al. (1989, 1993a,b) is of special interest. As noted before, reflectance spectra of suites of asphaltites, kerites, and anthraxolites show color characteristics similar to those of the low-albedo asteroids of the C, P, and D classes (Moroz et al. 1991, 1992), even though the strong band in many of these materials at 2.285 μm does not fit the Pholus spectrum. All other dark Solar System bodies studied so far, with the possible exceptions of two comets[1], show no distinct absorption bands (e.g., Luu et al. 1994, Barucci et al. 1994, Owen et al. 1995). However, as improving technology expands our ability to study yet fainter and more distant bodies in the outer Solar System, with the discovery of new diagnostic spectral features, the spectral properties of terrestrial organics can provide a further basis for comparative compositional studies.

Footnote 1   Cruikshank et al. (1991) reported absorption bands in some asteroids, the dark hemisphere of Iapetus, the rings of Uranus, and two comets, and proposed the identification of the CN bond in solid organic materials. The astronomical data were drawn from various published and unpublished sources. Since the

publication of that paper, spectra of higher quality of the same
(and other) asteroids and the dark hemisphere of Iapetus have
shown that the apparent absorption bands in the earlier data were
spurious. The two comets, Panther (1981 II) and Bowell (1982 I),
cannot be observed again, so the published spectra by Jewitt et
al. (1982), which appear to show a strong absorption band at 2.26
μm, must be considered valid. The reality of an absorption band
in the rings of Uranus remains ambiguous.

END FOOTNOTE

In the photovisual spectral region, as Moroz et al. (1991, 1992)
and Cloutis et al. (1994) found, the presence of both aliphatic
and aromatic groups is needed to provide red colors to the
asphaltite-like organics, but variations in the exact shape and
slope of the reflectance spectra of these materials are to be
expected in materials that are inherently complex mixtures of
diverse composition and structure. Recall that Titan tholin
consists of mostly aliphatic hydrocarbons.

DISCUSSION

What does the new information about the composition of Pholus
tell us about its origin, the chemical processes its surface has
undergone, and its relationship to Kuiper Belt planetesimals,
comets, and the dark asteroids of the Main Belt and the Jovian
Trojan populations?

Turning first to low-albedo asteroids at Jupiter's heliocentric
distance (the Trojan populations) and in the asteroid Main Belt,
we note that the colors (0.5-2.5 μm) of these bodies are either
neutral (flat) or red (upward sloping to longer wavelength) to
varying degrees (e.g., Luu et al. 1994, Barucci et al. 1994).
However, none of the reddest asteroids are even approximately as
red as Pholus (Mueller et al. 1992). Similarly, the colors of
comets in various stages of activity are never as red as Pholus

(Hartmann et al. 1986, Mueller et al. 1992, Jewitt and Meech 1988).

The short dynamical lifetime of Pholus in its present orbit (e.g., Levison and Duncan 1993), plus its nearly unique color and spectral properties, strongly suggest that it recently entered the planetary zone from the Kuiper Disk of planetesimals. Because the Kuiper Disk is the source of the low-inclination comets, and because of the compositional similarities of Pholus to comets, it is reasonable to conclude that Pholus is a primitive planetesimal that has not yet experienced large-scale sublimation or chemical processing through heating by the Sun. Instead, it has spent all but the last 10^6 to 10^7 years of its existence in the frozen state beyond about 40 AU from the Sun.

We assert that the surface of Pholus is rich in complex carbon compounds, and that in this paper we have shown spectral evidence that small, light hydrocarbons, methanol and/or its photolytic products, as well as H_2O ice, occur on the exposed surface. These complex organic molecules have two basic sources. First, about one-half of the material of the molecular cloud from which the Solar System formed consisted of carbon and organic-rich grains, if that molecular cloud was typical of others in the Galaxy (Tielens and Allamandola 1987). Second, after the formation of Pholus as a solid planetesimal, irradiation by ultraviolet photons, solar wind particles, and cosmic rays continued to affect the organic chemistry of the upper several meters of the crust or regolith. A third potential source arises from the interaction of Pholus with organic and other material in the interstellar medium, including other giant molecular clouds, as the Solar System moved through the Galaxy for 4.5 Gy.

Concerning the material from which Pholus condensed, there is abundant evidence from comets, meteorites, and interplanetary dust particles that much of the original organic matter in the outer solar nebula was retained during the planetesimal building phase of the Solar System's origin, and that much of the

22

incorporated material survived without melting or vaporization. Thus, Pholus began with an abundant inventory of complex organic molecules that resided on the interstellar grains from which it formed. The nature of the organic matter from which Pholus formed is revealed by the dust in the interstellar medium, particularly that matter in the dense molecular clouds. The dust component of the clouds consists of a mix of silicate grains (whose spectral signatures can be seen), and grains of organic solids composed of refractory material (polycyclic aromatic hydrocarbons, photolytic residues such as $(CH_2)_6N_4$ and HCOH, etc.), and volatile ices of H_2O, CO, alkanes, CH_3OH, OCS, H_2, XCN, etc.

Among those processes affecting the chemistry of Pholus after its formation, we consider only solar heat, the ultraviolet solar radiation and the flux of galactic cosmic rays (GCR); the solar wind may have been blocked by the heliopause, if Pholus' original position in the Kuiper Disk was beyond about 50 AU.

Solar ultraviolet at the heliocentric distances of bodies in the Kuiper Disk is weak (for ≤ 1500 A, the flux is $\tilde{} 10^{-3}$ erg cm^{-2} sec^{-1}), but the timescale is long; in 4.5 Gy $\tilde{} 1.5 \times 10^{14}$ erg cm^{-2} was deposited. This short wavelength ultraviolet, although it penetrates very little into the surface, is clearly capable of inducing chemical changes in organics and in ices. Experience with ultraviolet irradiation of carbon-bearing ices in the laboratory (e.g., Thompson et al. 1987) shows that as the radiation dose increases, an initially neutral-colored and high-albedo ice becomes red as the violet albedo decreases. Further irradiation gradually reduces the albedo at all wavelengths, and ultimately the material becomes very dark, neutral in color, and spectrally featureless. The details of the changes depend upon the radiation source (UV, ions, particles, etc.) and exposure time, the ice composition, temperature, etc., but the basic process involves the break-up of individual molecules into fragments that recombine to form more complex molecules and polymers (Khare et al. 1989, 1993). These materials have strong

charge-transfer electronic bands that absorb most in ultraviolet but extend to visible wavelengths. Hydrogen is removed from the material during the irradiation, and the end state is a mass of macromolecular carbon that is depleted of hydrogen. Titan tholin is produced initially in this way (corona discharge) from a mixture of gases, but the chemical processing is grossly similar to that in an ice, and the tholin is an intermediate step in the production of what, with continued irradiation (especially with a higher energy component), would become mostly carbon. In this sense, the extended irradiation processing of hydrocarbon ices is somewhat similar to the thermal processing of terrestrial biological matter toward oil, kerogen, and graphite. The principal difference is that the laboratory experiments produce mostly aliphatic organics and complex polymers, natural terrestrial organics are dominated by aromatic structures, and meteoritic organics contain a large fraction of cycloalkanes and hydrous alteration products (e.g., amino and carboxylic acids).

Even with generous estimates of surface overturn through impact gardening, there was ample time and radiation to effect surface organic chemistry by solar ultraviolet light, and to a depth characteristic of the small-scale impact gardening process.

Galactic cosmic rays (GCR) have their maximum flux in the energy range 10 MeV to 10 GeV. The total energy deposition will be about 9×10^{-3} ergs cm^{-2} sec^{-1}, or 1.3×10^{15} ergs cm^{-2} over age of Solar System. For 1 GeV GCR, the deposition of the energy will occur over about the upper 10 meters of surface (depending upon the density), for an accumulated flux of 1.3×10^{12} ergs cm^{-3}. The efficiency of production of complex molecules is about 1×10^{-3} eV^{-1} (Schutte 1988). Using this efficiency factor, and following the model for production of the complex organic molecules (>50 amu) in the crust and interior of Comet P/Halley (Mitchell et al. 1992), in 4.5 Gy, the number fraction of these molecules relative to H_2O is ˜0.1 at the surface and ˜0.0005 at a depth of 100 m. Mitchell et al. (1992) observed ˜10^{-3} complex molecules per H_2O in the coma dust of P/Halley, and reasoned that

production of these molecules by GCR after the accretion of the comet's nucleus was insufficient to account for this number density. The complex molecules therefore were included in the material from which the nucleus accreted.

The same reasoning pertains to Pholus and other planetesimals still in the Kuiper Disk and the Oort Cloud; their organic inventory was largely set by the material from which they accreted, and although it has been altered to some depth by the GCR flux in 4.5 Gy, the basic inventory has not changed.

What, then, causes the difference between Pholus and the low-albedo asteroids and comets in the inner Solar System? The only remaining known factor, after UV and GCR are accounted for, is the ambient heat provided by the present Sun and the heating events in the inner Solar System from the early Sun. The presence of differentiated asteroids and the hydrothermal chemical alteration of other asteroids, all revealed in the meteorite record, demonstrates the reality of those early heating events, although the exact phyical causes continue to be debated. In any event, objects in the Kuiper Disk did not experience the heating experienced by objects in the inner planetary zone.

Do other Solar System bodies show evidence for organic solids? The low albedo and neutral or red colors (0.3-1.5 μm) of comets and certain classes of asteroids (C, P, and D) have long been thought to indicate the presence of macromolecular carbon-bearing molecules in their surface materials (e.g., Cruikshank 1987, 1989; Owen et al. 1995), but with one unconfirmed exception (Cruikshank and Brown 1987) they show no spectral absorption features diagnostic of the composition of those carbon-bearing molecules. In particular, the band we see in the Pholus spectrum at 2.27 μm is not seen in any other plausible candidate object to date (e.g., Luu et al. 1994, Barucci et al. 1994). It is reasonable to conclude that the organic signatures in the nuclei of comets and the surfaces of C, P, and D asteroids have been removed by heating and devolatilization, leaving very large

molecules (>500 amu) and elemental carbon, both of which have very high opacity and no diagnostic spectral bands when seen in diffuse reflectance in the accessible spectral regions.

OBJECT 1993 HA$_2$

The object designated 1993 HA$_2$ was discovered some 15 months after Pholus. Its orbital similarity to Pholus, with a perihelion beyond Saturn and aphelion inside Pluto's orbit, suggests a similar origin and dynamical history. 1993 HA$_2$ is somewhat fainter than Pholus, but the photometry by Davies and Tholen (1996) shows that this object is only slightly less red in color. Their results for five individual observations, which can be compared with the Pholus photometry in Table II, are V-J = 2.07 ±0.4 and V-K = 2.27 ±0.4. 1993 HA$_2$ is not sufficiently bright to permit spectroscopy in the near-IR, but its color and dynamical similarity to Pholus invites speculation that its surface is also rich in primitive organic molecules.

CONCLUSIONS

The extraordinary red color and the unique near-IR spectral signature of Pholus are explained by the presence of organic molecules, H$_2$O ice, and carbon on its surface. Both the red color and the 2.27-μm absorption band suggest the presence of small hydrocarbon molecules, produced in both cases by the ultraviolet (or corona discharge) irradiation of very simple molecules (CH$_4$, H$_2$O, CO, NH$_3$, N$_2$, CH$_3$OH). The photolytic products of these simple molecules are larger molecules ($\leq$~300 amu) which are relatively refractory and stable, but which would further reduce to elemental carbon and macromolecular carbon-bearing molecules (>500 amu) in the presence of significant heating. We conclude that most of the organic molecules present on Pholus' surface are the partially processed remnants of the original inventory of material, formed in the interstellar medium, from which Pholus and other planetesimals accreted in what is now the Kuiper Disk.

If Pholus remains in its present orbit or moves closer to the Sun, its surface materials will begin to volatilize and form a coma, and the small organic molecules will lose hydrogen and be transformed into a less red-colored and spectrally featureless macromolecular carbonaceous mass. Object 2060 Chiron, which lies in a planet-crossing orbit similar to that of Pholus, represents this stage of the evolution of such a body. Chiron has a coma (Hartmann et al. 1990; Meech and Belton 1990) and a low-albedo, spectrally featureless continuum reflectance out to 2.5 μm (Luu et al. 1994). Comet P/Schwassmann-Wachmann 1 is similar to Chiron in terms of its a persistent and episodically active coma (Jewitt 1990) and its spectral reflectance (Meech et al. (1993); Owen et al. 1995).

APPENDIX A [The Methanol Spectrum]

Laboratory measurements of the spectrum of solid methanol were made at the Extraterrestrial Ice Facility, at the Jet Propulsion Laboratory. Spectra were measured between 1 and 5 microns at temperatures between 90 and 120 K, a range which includes the temperature at which a solid phase transition occurs.

A thin film of methanol was formed by spraying gaseous methanol onto a sapphire window, held at T = 90K, at a rate of approximately 0.07 microns/minute. The exact thickness of the film was determined by measuring interference fringes produced by a laser whose beam was directed onto the area where the film was forming. The film thickness for the measurements presented here was 13.67 microns.

The temperature of the window was maintained by a combination of cooling, provided by contact with a cold finger, and warming, from a heater, attached to the window. The temperature of the window was known to an accuracy of ±0.5 K during the measurements.

27

A spectrum was taken at 90 K and then the temperature of the system was incrementally raised to 120 K. Spectra taken at intermediate temperatures show that a change in the shape of some of the spectral bands occured between 100 and 105 K, probably corresponding to a phase transition of solid methanol that occurs in this temperature range.

Values of the real and imaginary indices of refraction were determined by using the subtractive-Krammers-Kronig integral (e.g., Warren 1984).

APPENDIX B [The Lab Spectrometer]

Experimental measurements of the spectral reflectance of our laboratory samples in the 0.25 to 2.5 μm region were made at room temperature using a dual-beam, dual-monochrometer, dispersive Perkin-Elmer Lambda 9 UV/VIS/NIR Spectrophotometer equipped with a Labsphere DRTA-9 integrating sphere. The integrating sphere is coated with Spectralon, a high reflectance material (the spectral reflectance is greater than 95% over the entire wavelength region), and disks of the same material were used for the reference beam and the instrument background correction. The 6-inch diameter sphere has entrance ports to admit the sample and reference beams.

The sample is positioned opposite the entrance port to make reflectance measurements in an integrating sphere. The light scattered into all angles of the backward hemisphere is collected by the sphere and measured by the detector after multiple internal reflections. Internal reflections against the diffuse surface of the integrating sphere average out the surviving angular components of the scattered or reflected light before it reaches the detector.

The measured reflectance data could be corrected to obtain the absolute reflectance of the samples. This small correction factor, the diffuse spectral reflectance of the coating material,

accounts for absorption of the integrating sphere's coating material at the reference beam reflectance port. However, data provided by the manufacturer indicate that the reflectance of the coating material is greater than 96 % at all measurement wavelengths, so this correction is negligible at most wavelengths, ranging to at most a 4% decrease in reflectance at the wavelengths where the coating is most highly absorbing.

REFERENCES

Allamandola, L. J., S. A. Sandford, and G. J. Valero 1988. Photochemical and thermal evolution of interstellar/precometary ice analogs. **Icarus 76**, 225-252.

Barnes, A. J., and H. E. Hallam 1970. Infrared cryogenic studies: Part 4--Isotopically substituted methanols in argon matricies. **Trans. Faraday Soc. 66**, 1920-1931.

Barucci, M. A., M. Lazzarin, T. Owen, C. Barbieri, and M. Fulchignono. 1994. Near-infrared spectroscopy of dark asteroids. **Icarus 110**, 287-291.

Bell, J. F. III, J. B. Pollack, T. R. Geballe, D. P. Cruikshank, and R. Freedman 1994. Spectroscopy of Mars from 2.04 to 2.44 μm during the 1993 opposition: Absolute calibration and atmospheric vs mineralogic origin of narrow absorption features. **Icarus 111**, 106-123.

Binzel, R. 1993. The optical spectrum of 5145 Pholus. **Icarus**

99, 238-240.

Bernstein, M. P., S. A. Sandford, L. J. Allamandola, and S. Chang 1994. Infrared spectrum of matrix-isolated hexamethylenetetramine in Ar and H_2O at cryogenic temperatures. **J. Phys. Chem 98**, 12206-12210.

Bernstein, M. P., S. A. Sandford, L. J. Allamandola, S. Chang, and M. A. Scharberg 1995. Organic compounds produced by photolysis of realistic interstellar and cometary ice analogs containing methanol. **Astrophys. J. 454**, 327-344.

Bockelée-Morvan, D., P. Colom, J. Crovisier, D. Despois, and G. Paubert 1991. Microwave detection of hydrogen sulphide and methanol in comet Austin (1989c1). **Nature 350**, 318-320

Buie, M. J., and S. J. Buss 1992. Physical observations of (5145) Pholus. **Icarus 100**, 288-294.

Campins, H., G. H. Rieke, and M. J. Lebofsky 1985. Absolute calibration of photometry at 1 through 5 μm. **Astron. J. 90**, 896-899.

Clark, R. N., G. A. Swayze, A. J. Gallagher, T. V. V. King, and W. M. Calvin 1993. The U.S.G.S. Digital Spectral Library: Version 1: 0.2 to 3.0 μm. U.S. Geological Survey Open File Report 93-592.

Cloutis, E. A. 1989. Spectral reflectance properties of hydrocarbons: Remote sensing implications. **Science 245**, 165-168.

Cloutis, E. A., M. J. Gaffey, and T. F. Moslow 1994. Spectral reflectance properties of carbon-bearing materials. **Icarus 107**, 276-287.

Cronin, J. R., S. Pizzarello, and D. P. Cruikshank 1989. Organic matter in carbonaceous chondrites, planetary satellites, asteroids, and comets. In **Meteorites and the Early Solar System**, J. F. Kerridge and M. S. Matthews, Eds. Univ. Arizona Press, pp 819-857.

Cruikshank, D. P. 1987. Dark matter in the Solar System. **Adv. Space Res. 7**, (5)109-120.

Cruikshank, D. P. 1989. Dark surfaces of asteroids and comets: Evidence for macromolecular carbon compounds. **Adv. Space Res. 9**, (2)65-71.

Cruikshank, D. P., L. J. Allamandola, W. K. Hartmann, D. J. Tholen, R. H. Brown, C. N. Matthews, and J. F. Bell 1991. Solid CN bearing material on outer Solar System bodies. **Icarus 94**, 345-353.

Cruikshank, D. P., and J. F. Kerridge 1992. Organic material in asteroids, meteorites, and planetary satellites. In **Exobiology**

in Solar System Exploration, G. Carle, D. Schwartz, and J. Huntington, eds. pp 159-175. NASA SP-512.

Cruikshank, D. P., L. V. Moroz, T. R. Geballe, C. M. Pieters, and J. F. Bell, III 1993a. Asphaltite-like organics on planetesimal 5145 Pholus. **Bull. A. A. S. 25**, 1125-1126 (abstract).

Cruikshank, D. P., T. L. Roush, T. C. Owen, T. R. Geballe, C. de Bergh, B. Schmitt, R. H. Brown, and M. J. Bartholomew 1993b. Ices on the surface of Triton. **Science 261**, 742-745.

Cruikshank, D. P., and R. H. Brown 1987. Organic matter on asteroid 130 Elektra. **Science 238**, 183-185

Davies, J. K., and M. V. Sykes 1992. 5145-1992 AD. **IAU Circular 5480** (20 March).

Davies, J. K., and D. J. Tholen 1996. Infrared observations of distant asteroids. In **Completing the Inventory of the Solar System**, T. W. Rettig, Ed. Astron. Soc. Pacific Conf. Series, pp xx-xx (in press).

Davies, J. K. et al. 1993a. 5145 Pholus. **IAU Circular** 5698 (27 January).

Davies, J. K., M. V. Sykes, and D. P. Cruikshank 1993b. Near-infrared photometry and spectroscopy of the unsual minor planet 5145 Pholus (1992AD). **Icarus 102**, 166-169.

Davies, J. K., T. Geballe, D. Cruikshank, T. Owen, and C. deBergh 1995. Comet C/1995 O1. **IAU Circular** 6225 (11 September).

Davies, J. K., D. P. Cruikshank, T. Roush, T. C. Owen, M. J. Bartholomew, C. deBergh, and T. R. Geballe 1996. Water ice on Comet Hale-Bopp, C/1995 O1. **Icarus** (nearly submitted).

Ehrenfreund, P., J. J. Boon, J. Commandeur, C. Sagan, W. R. Thompson, and B. N. Khare 1994. Analytical pyrolysis experiments of Titan aerosol analogues in preparation for the Cassini-Huygens mission. **Adv. Space Res. [in press**].

Fink. U., M. Hoffmann, W. Grundy, M. Hicks, and W. Sears 1992. The steep red spectrum of 1992 AD: An asteroid covered with organic material? **Icarus 97**, 145-149.

Hanel, R., B. Conrath, F. M. Flasar, V. Kunde, W. Maguire, J. Pearl, J. Pirraglia, R. Samuelson, L. Herath, M. Allison, D. Cruikshank, D. Gautier, P. Gierasch, L. Horn, R. Koppany, and C. Ponnameruma 1981. Infrared observations of the saturnian system from Voyager 1. **Science 212**, 192-200.

Hapke, B. 1993. **Theory of Reflectance and Emittance Spectroscopy**, Cambridge Univ. Press, Cambridge. 455 pp.

Hartmann, W. K., D. J. Tholen, and D. P. Cruikshank 1986. The

relationship of active comets, "extinct" comets, and dark asteroids. **Icarus 69**, 33-50.

Hartmann, W. K., D. J. Tholen, K. J. Meech, and D. P. Cruikshank 1990. 2060 Chiron: Colorimetry and possible cometary behavior. **Icarus 83**, 1-15.

Hoban, S., M. J. Mumma, D. C. Reuter, M. DiSanti, R. R. Joyce, and A. Storrs 1991. A tentative identification of methanol as the progenitor of the 3.52 μm feature in several comets. **Icarus 93**, 122-134.

Hoffmann, M., U. Fink, W. M. Grundy, and M. Hicks 1993. Photometric and spectroscopic observations of 5145 Pholus. **J. Geophys. Res. 98**, 7403-7407.

Howell, E. S., R. Marcialis, R. Cutri, M. Nolan, L. Lebofsky, and M. Sykes 1992. 1992AD, **IAU Circular** 5449 **(12 February)**.

Howell, E. S. 1995. Probing asteroid composition using visible and near-infrared spectroscopy. Thesis, Univ. of Arizona, Tucson, 186 pp.

Huebner, W. F. 1987. First polymer in space identified in Comet Halley. **Science 237**, 628-630.

Jewitt, D. C. 1990. The persistent coma of comet P/Schwassmann-Wachmann 1. **Ap. J. 351**, 277-286.

Jewitt, D. C., B. T. Soifer, G. Neugebauer, K. Matthews, and G. E. Danielson 1982. Visual and infrared observations of the distant comets P/Stephan-Oterman (1980g), Panther (1980u), and Bowell (1980b). **Astron. J. 87**, 1854-1866.

Jewitt, D. C., and J. X. Luu 1995. The solar system beyond Neptune. **Astrophys. J. 109**, 1867-1876.

Jewitt, D. C., and K. J. Meech 1988. The absence of a color-distance trend in comets. **Astron. J. 96**, 1723-1730.

Khare, B. N., C. Sagan, E. T. Arakawa, F. Suits, T. A. Callcott, and M. W. Williams 1984a. Optical constants of organic tholin produced in a simulated Titanian atmosphere: From soft X-ray to microwave frequencies. **Icarus 60**, 127-137.

Khare, B. N., C. Sagan, W. R. Thompson, E. T. Arakawa, F. Suits, T. A. Callcott, M. W. Willams, S. Shrader, H. Ogino, T. O. Willingham, and B. Nagy 1984b. The organic aerosols of Titan. **Adv. Space Res. 4**, 59-68.

Khare, B. N., C. Sagan, H. Ogino, B. Nagy, C. Er, K. H. Schram, and E. T. Arakawa 1986. Amino acids derived from Titan tholins. **Icarus 68**, 176-184.

Khare, B. N., W. R. Thompson, B., G. J. P. T. Murray, C. F.

Chyba, C. Sagan, and E. T. Arakawa 1989. Solid organic residues produced by irradiation of hydrocarbon-containing H_2O and H_2O/NH_3 ices: Infrared spectroscopy and astronomical implications. **Icarus 79**, 350-361.

Khare, B. N., W. R. Thompson, L. Cheng, C. Chyba, C. Sagan, E. T. Arakawa, C. Meisse, and P. S. Tuminello 1993. Production and optical constants of ice tholin from charged particle irradiation of (1:6) C_2H_6/H_2O at 77 K. **Icarus 103**, 290-300.

Lacy, J. H., F. Baas, L. J. Allamandola, S. E. Persson, P. J. McGregor, C. J. Lonsdale, T. R. Geballe, and C. E. P. van de Bult 1984. 4.6 micron absorption features due to solid phase CO and cyano group molecules toward compact infrared sources. **Astrophys. J. 276**, 533-543.

Levison, H. F., and M. J. Duncan 1993. The gravitational sculpting of the Kuiper belt. **Astrophys. J. Let. 406**, L35-L38.

Luu, J., D. Jewitt, and E. Cloutis (1994). Near-infrared spectroscopy of primitive solar system objects. **Icarus 109**, 133-144.

Marsden, B. G. (1992) **IAU Circular** 5480 (20 March).

McDonald, G. D., W. R. Thompson, M. Heinrich, B. N. Khare, and C. Sagan 1994. Chemical investigation of Titan and Triton tholins. **Icarus 108**, 137-145.

Meech, K. J, and M. J. S. Belton 1990. The atmosphere of 2060 Chiron. **Astron. J. 100**, 11323-1338.

Meech, K. J., M. J. S. Belton, B. E. A. Mueller, M. W. Dicksion, and H. R. Li 1993. Nucleus properties of P/Schwassmann-Wachmann 1. **Astron. J. 106**, 1222-1236.

Mitchell, D. L., R. P. Lin, K. A. Anderson, C. W. Carlson, D. W. Curtis, A. Korth, H. Rème, J. A. Sauvard, C d'Uston, and D. A. Mendis. 1957. Evidence for chain molecules enriched in carbon, hydrogen, and oxygen in Comet Halley. **Science 237**, 626-628.

Mitchell, D. L., R. P. Lin, C. W. Carlson, A. Korth, H. Rème, and D. A. Mendis 1992. The origin of complex organic ions in the coma of Comet Halley. **Icarus 98**, 125-133.

Moroz, L. V., C. M. Pieters, and M. V. Akhmanova 1991. Spectroscopy of solid carbonaceous materials: Implications for dark surfaces of outer belt asteroids. **LPSC XXII**, 925-6.

Moroz, L. V., C. M. Pieters, and M. V. Akhmanova 1992. Why the surfaces of outer belt asteroids are dark and red. **LPSC XXIII**, 931-2.

Mueller, B. E. A., D. J. Tholen, W. K. Hartmann, and D. P. Cruikshank 1992. Extraordinary colors of asteroidal object

(5145) 1992 AD. **Icarus 97**, 150-154.

Mumma, M. J., P. R. Weissman, and S. A. Stern 1993. Comets and the origin of the solar system: Reading the Rosetta Stone. In **Protostars and Planets III**, E. H. Levy and J. I. Lunine, eds. Univ. of Arizona Press, pp 1177-1252.

Ockman, N. 1957. The infrared-spectra and Raman-spectra of single crystals of ordinary ice. Dissertation, Univ. Michigan, Ann Arbor, MI, 171 pp.

Owen, T. C., D. P. Cruikshank, C. de Bergh, and T. R. Geballe 1995. Dark matter in the outer Solar System. **Adv. Space Res. 16**, (2)41-49.

Owen, T. C., D. P. Cruikshank, T. Roush, T. R. Geballe, C. deBergh, and M. J. Bartholomew 1996. Water ice on Phoebe. **Icarus** (nearly submitted)

Papoular, R., J. Conard, M. Giuliano, J. Kister, and G. Mille 1989. A coal model for the carriers of the unidentified IR bands. **Astron. Astrophys 217**, 204-208.

Papoular, R., J. Breton, G. Gensterblum, I. Nenner, R. J. Papoular, and J.-J. Pireaux 1993a. The vis/UV spectrum of coals and the interstellar extinction curve. **Astron. Astrophys 270,** L5-L8.

Papoular, R., K. Ellis, O. Guillois, C. Reynaud, and I. Nenner 1993b. New developments of the coal model of interstellar dust. **J. Chem. Soc. Faraday Trans. 89**, 2289-2295.

Pendleton, Y. J. 1993. Organics in the diffuse interstellar medium. In **Astronomical Infrared Spectroscopy: Future Observational Directions**, S. Kwok, ed. Astron. Soc. Pacific Conf. Series, Vol. 41, 171-179.

Pendleton, Y. J. 1995. Laboratory comparisons of organic materials to interstellar dust and the Murchison meteorite. **Planet. Space Sci. 43**, 1359-1364.

Pendleton, Y. J., S. A. Sandford, L. J. Allamandola, A. G. G. M. Tielens, and K. Sellgren 1994. Near-infrared absorption spectroscopy of interstellar hydrocarbon grains. **Astrophys. J. 437**, 683-696.

Pendleton, Y. J., A. G. G. M. Tielens, and A. T. Tokunaga 1996. Nitriles in protostellar regions. **Astrophys. J.** (submitted).

Quirico, E., and B. Schmitt 1996. Near infrared spectroscopy of simple hydrocarbons and carbon oxides diluted in solid N_2 and as pure ices: Implication for Triton and Pluto. **Icarus** (submitted).

Roush, T. L., J. B. Pollack, F. C. Witteborn, J. D. Bregman, and J. P. Simpson 1990. Ice and minerals on Callisto: A reassessment

of the reflectance spectra. **Icarus 86**, 355-382.

Roush, T. L. 1994. Charon: More than water ice? **Icarus 108**, 243-254.

Roush, T. 1996. Near-ir (0.8-2.5 μm) optical constants of water ice at 100K. Lunar Planet. Sci. Conf. XXVII, Lunar and Planetary Institue, Houston, TX, to be submitted.

Sandford S. A., L. J. Allamandola, A. G. G. M. Tielens, K. Sellgren, M. Tapia, and Y. Pendleton 1991. The interstellar C-H stretching band near 3.4 microns: Constraints on the composition of organic material in the diffuse interstellar medium. **Astrophys. J. 371**, 607-620.

Sandford, S. A., and L. J. Allamandola 1993. Condensation and vaporization studies of CH_3OH and NH_3 ices: Major implications for astrochemistry. **Astrophys. J. 417**, 815-825. (methanol spectrum in Figs 2 and 3.)

Sagan, C., and B. N. Khare 1979. Tholins: Organic chemistry of interstellar grains and gas. **Nature 227**, 102-107.

Sagan, C., B. N. Khare, and J. S. Lewis 1984. Organic matter in the Saturn system. In **Saturn** (T. Gehrels and M. S. Matthews, Eds.), pp 788-807. Univ. of Arizona Press, Tucson.

Schmitt, B., and E. Quirico 1992. Laboratory data on near-infrared spectra of ices of planetary interest. **Bull. Amer. Astron. Soc. 24**, 968 (abstract).

Schutte, W. A. 1988. **The Evolution of Interstellar Organic Grain Mantles.** Ph.D. thesis, University of Leiden, The Netherlands.

Scotti, J. V. 1992. **IAU Circ. 5434**, 23 January.

Strazzulla, G., A. C. Castorina, and M. E. Palumbo 1995. Ion irradiation of astrophysical ices. **Planet. Space Sci. 43**, 1247-1251.

Tegler, S. C., D. A. Weintraub, L. J. Allamandola, S. A. Sandford, T. W. Rettig, and H. Campins 1993. Detection of the 2165 inverse centimeter (4.619 micron) XCN band in the spectrum of L1551 IRS 5. **Astrophys. J. 411**, 260-265.

Tegler, S. C., D. A. Weintraub, T. W. Rettig, Y. J. Pendleton, D. C. B. Whittet, and C. A. Kulesa 1995. Evidence for chemical processing of precometary ice grains in circumstellar environments of pre-main-sequence stars. **Astrophys. J. 439**, 279-287.

Thompson, W. R., B. G. J. P. T. Murray, B. N. Khare, and C. Sagan 1987. Coloration and darkening of methane clathrate and other ices by charged particle irradiation: Applications to the outer

solar system. **J. Geophys. Res. 92**, 14,933-14,947.

Thompson, W. R., T. J. Henry, J. M. Schwartz, B. N. Khare, and C. Sagan 1991. Plasma discharge in N_2+CH_4 at low pressures: Experimental results and applications to Titan. **Icarus 90**, 57-73.

Tielens, A. G. G. M., and L. J. Allamandola 1987. Evolution of interstellar dust. In **Physical Processes in Interstellar Clouds**, G. E. Morfill and M. Scholer, Eds. Reidel, Dordrecht, pp 333-376.

Van Dishoeck, E. F., G. A. Blake, B. T. Draine, and J. I. Lunine 1993. The chemical evolution of protostellar and proplanetary matter. In **Protostars and Planets III**, E. Levy and J. I. Lunine, Eds. Arizona, Tucson, pp 163-241.

Warren, S. G. 1984. Optical constants of ice from the ultraviolet to the microwave. **App. Opt. 23**, 1206-1225.

Wilson, P. D., C. Sagan, and W. R. Thompson 1994. The organic surface of 5145 Pholus: Constraints set by scattering theory. **Icarus 107**, 288-303.

FIGURE CAPTIONS

Figure 1. (a) The first version of the composite spectrum of Pholus (see text), with representative error bars. Between 0.4 and 1.0 μm, three data sets are shown; the continuous line is from Binzel 1992, and the other symbols are identified in the key. The solid hexagons are the average values of JHK photometric points, as discussed in the text. (b) The composite spectrum of Pholus without the photometric points, error bars, and the points by Mueller et al. 1992, for clarity. The dashed line is the model consisting of Titan tholin, H_2O ice, CH_3OH ice, and carbon black, as discussed in the text.

Figure 2. (a) The second version of the composite spectrum of Pholus (see text), including data at 1.2 μm. Otherwise, as in Fig. 1a. (b) As Fig. 1b, but with the second version of the composite spectrum of Pholus.

Figure 3. The spectrum of Pholus and our model, as in Figure 2b(ordinate on the left), with the measured reflectance spectrum of powdered hexamethylenetetramine (HMT) and a computed (geometric albedo) spectrum of CH_3OH ice at *** K (5 um grain size). The ordinate on the right corresponds to the HMT and CH_3OH spectra; the spectrum of CH_3OH is offset downward by 0.1 for clarity.

Figure 4. The normalized spectrum of Pholus obtained by Luu et al. (1994), with the model presented in this paper (offset upward by 0.1).
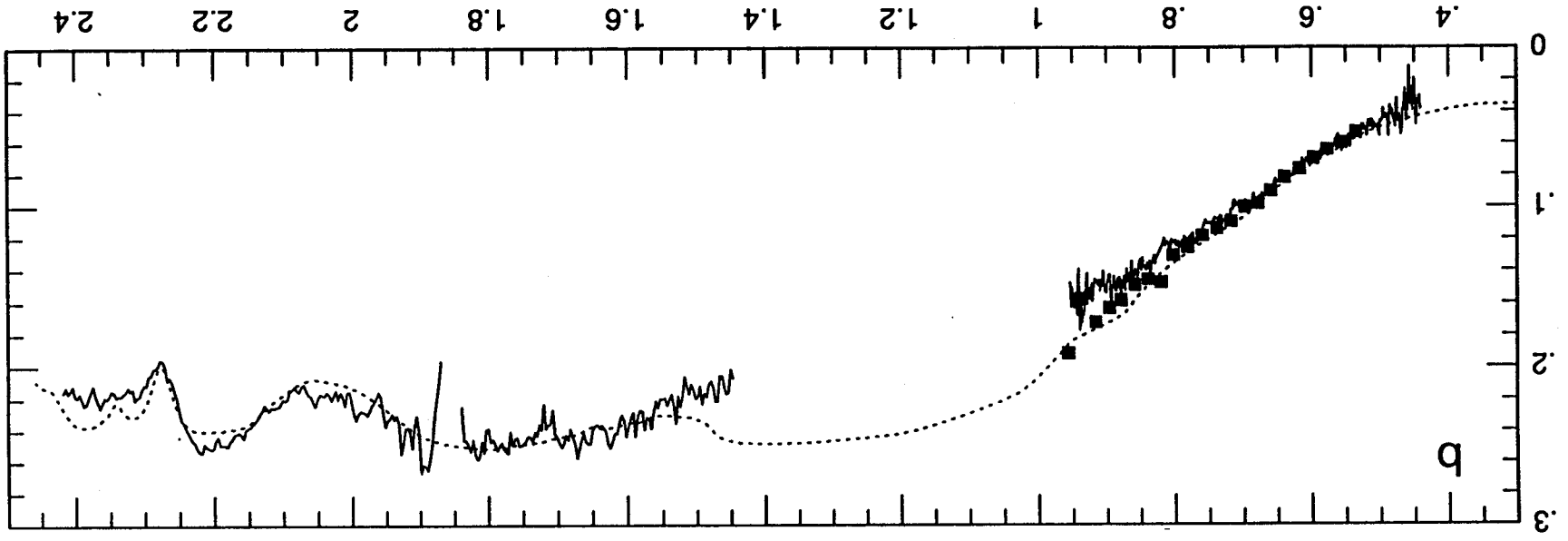
Figure 5. Synthesis of hexamethylenetetramine (HMT) from CH_3OH,

and the decomposition products of HMT. From Bernstein et al. (1995).

Figure 6. Laboratory reflectance spectra of HMT, piperazine (offset downward by 0.1), and paraformaldehyde (POM) (offset downward by 0.2).

Figure 7. The composite spectrum of Pholus (second version) presented in this work, with our computation of the Wilson et al. (1994) model. See text.
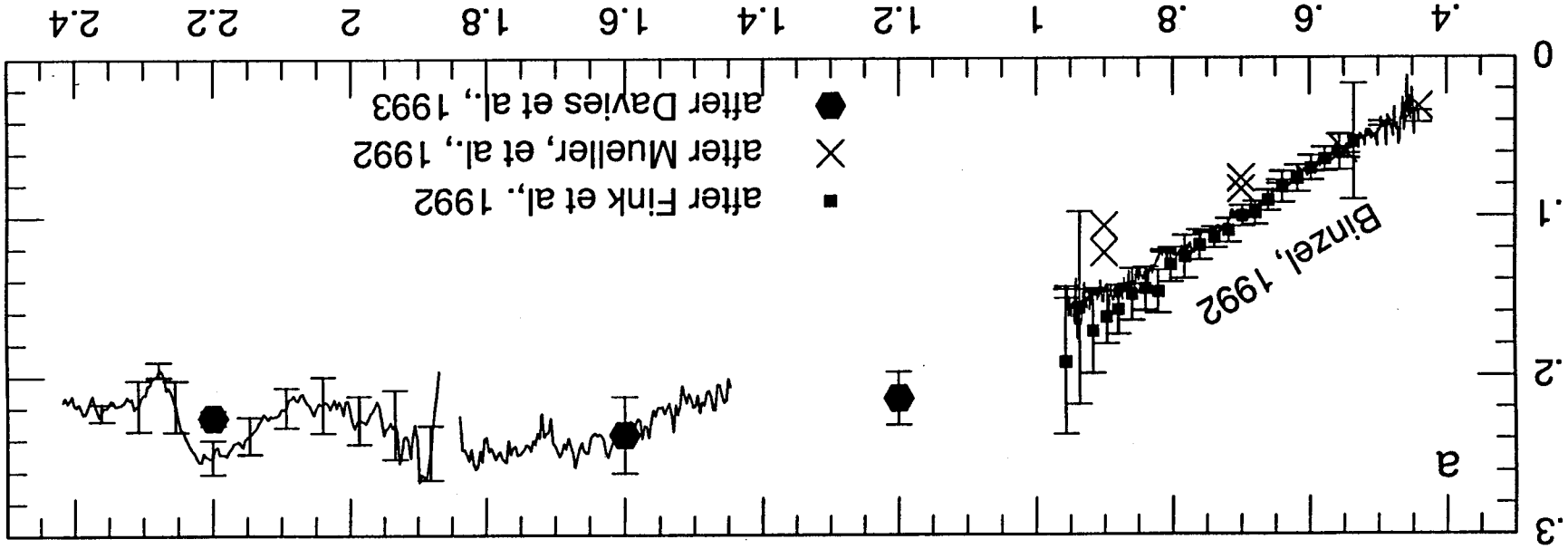
Fig. 1

(The figure shows two panels (a and b) plotting Geometric Albedo versus Wavelength (μm). The wavelength axis ranges from .4 to 2.4 μm. The geometric albedo axis ranges from 0 to .3.)

Panel b (top): labeled "b", showing Geometric Albedo vs Wavelength (μm)

Panel a (bottom): labeled "a", showing Geometric Albedo vs Wavelength (μm)

Legend:
- ⬢ after Davies et al., 1993
- × after Mueller, et al., 1992
- ▪ after Fink et al., 1992
- Binzel, 1992

Fig. 2

Hexamethylene tetramine

Methanol ice

model

Pholus

Wavelength (μm)

Geometric Albedo

Fig. 2

model

Pholus, after Luu et al., 1994

Scaled Reflectance

Wavelength (μm)

Fig.

4

(A) CH_3OH $\xrightarrow[\text{(-H}_2\text{)}]{\text{U V}}$ $CH_2=O$ $\xrightleftharpoons{\text{+ NH}_3}$ $CH_2=NH$ $+$ H_2O

Methylene*imine*

(B) $3\ CH_2=NH$ $\rightleftharpoons$

Methylene*imine*

Hexahydro-1,3,5-Triazine
(Trimer of Methylene*imine*)

(C)

Hexahydro-1,3,5-Triazine
(Trimer of Methylene*imine*)

$+$ $3\ CH_2=O$ $\rightleftharpoons$

1,3,5- Trihydroxymethyl
Hexahydro-1,3,5-Triazine

(D)

1,3,5- Trihydroxymethyl
Hexahydro-1,3,5-Triazine

$+$ NH_3 $\xrightarrow{\text{(-3H}_2\text{O)}}$

HMT

$\xrightarrow{\text{Heat}}$ Methylamines (R_2NCH_3)
Methane (CH_4)
Ammonia (NH_3)
Oxides of carbon $(CO,\ CO_2)$
Oxides of nitrogen $(R_3N=O)$

$\xrightarrow{\text{UV}}$ Methylamines (R_2NCH_3)
Methane (CH_4)
Ammonia (NH_3)
Oxides of carbon $(CO,\ CO_2)$
Oxides of nitrogen $(R_3N=O)$
Carbodiimides $(RN=C=NR)$
Nitriles $(RNC\ \&\ RCN)$

$\downarrow H_3O^+$

Amino Acids $(H_2N-R-CO_2H)$
Ammonia (NH_3)
Formaldehyde (H_2CO)
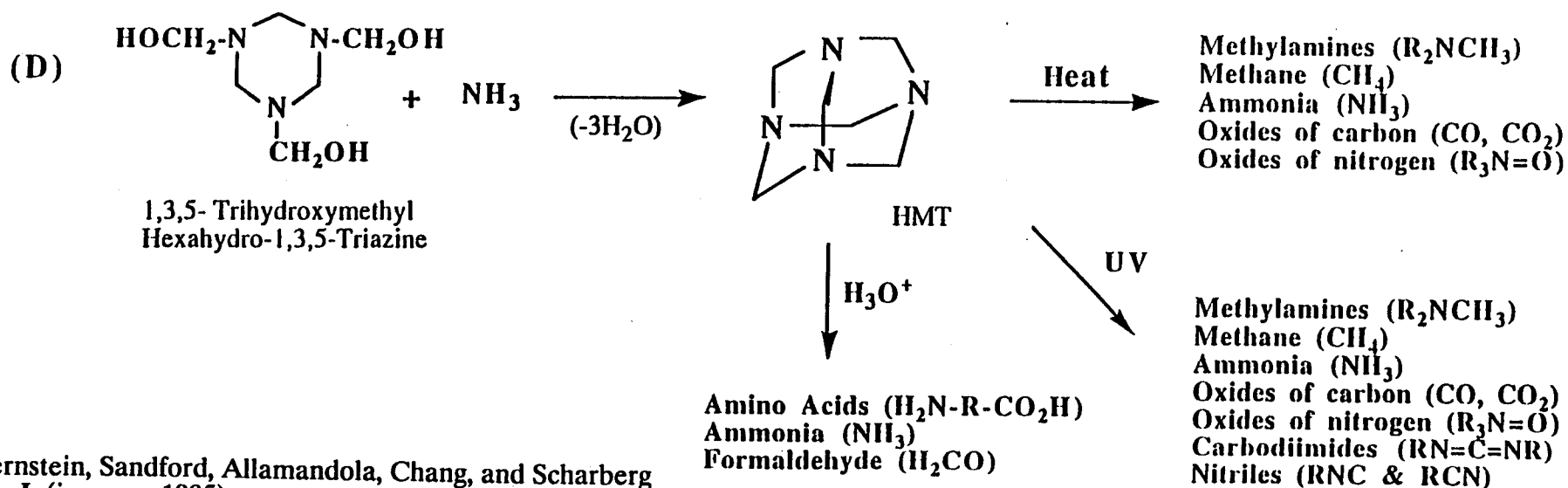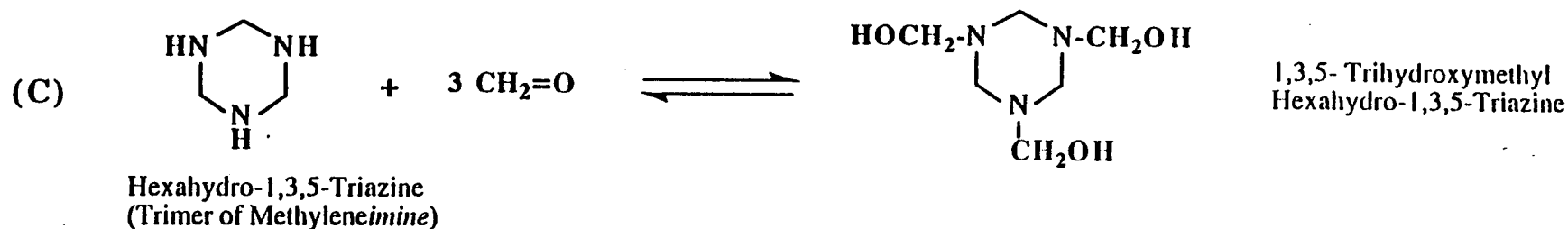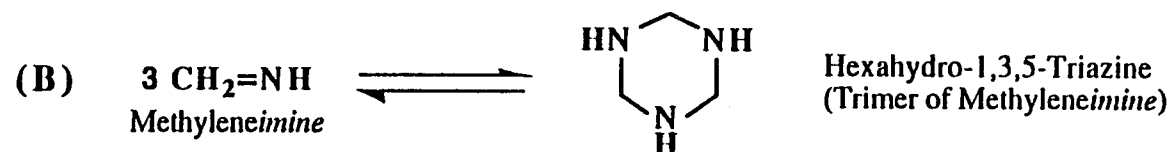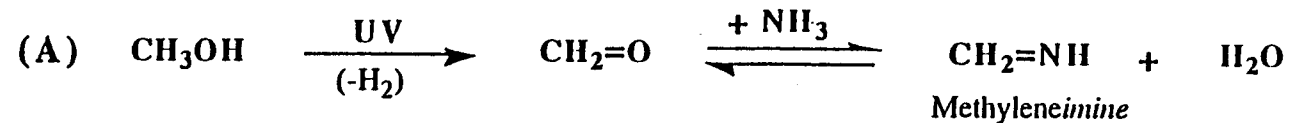
Bernstein, Sandford, Allamandola, Chang, and Scharberg
Ap. J. (in press, 1995)

Fig.

Fig. 6
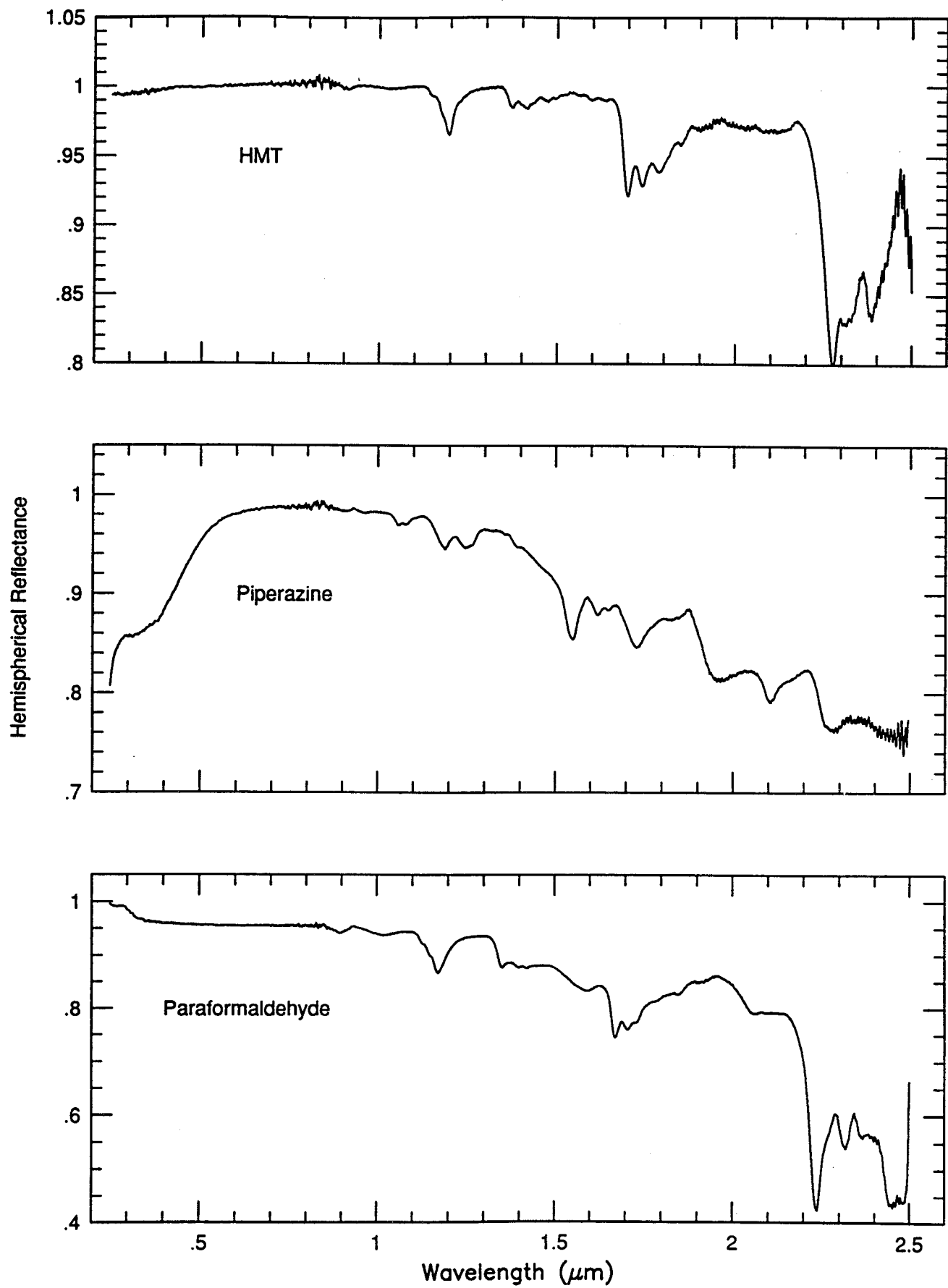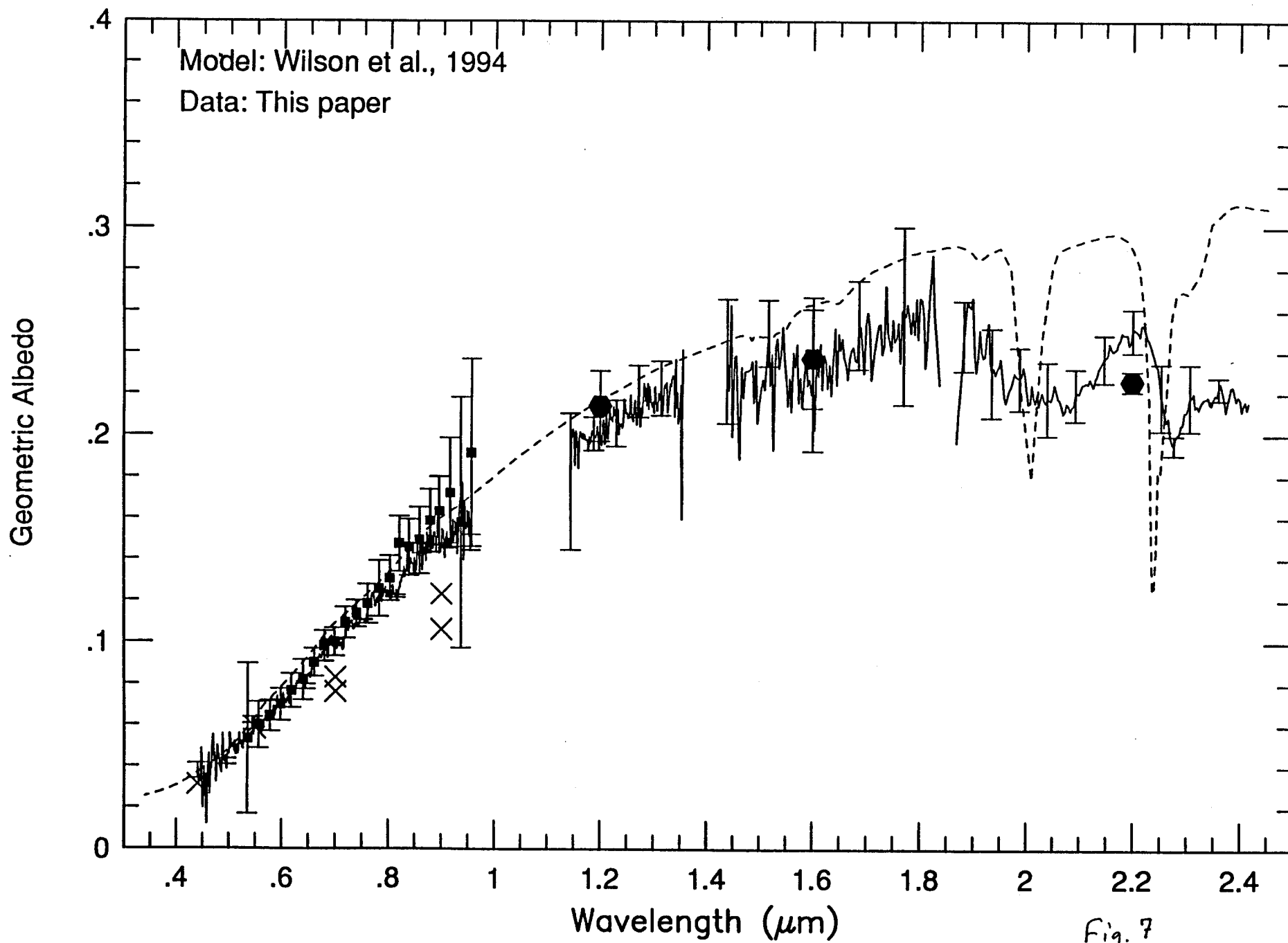
Fig. 7

Table I

Spectra of Pholus with UKIRT/CGS4

Date UT	R AU	Del AU	i deg	Region covered $\lambda\lambda$ μm	Quality	Primary Standard
1992 Mar 26.3	8.724	8.323	6.14	1.45-2.43	Good	BS2890
1993 Feb 4.4	8.959	7.982	0.94	2.04-2.46	Excellent	BS4030
1994 Apr 19.2	9.595	9.088	5.29	1.14-1.82	V. Good	BS4027
1995 May 11.2	10.378	9.973	5.21	1.60-2.27	Good	BS4345
1995 May 13.2	10.382	10.006	5.27	1.88-2.50	V. Good	BS4345
1995 May 15.2	10.387	10.040	5.33	1.88-2.50	Good	BS4345

Table II

Photometry of Pholus

UT Date (1992)	R AU	Delta AU	Phase deg	V	V-J	V-H	V-K	Source
Feb 22.148	8.71	7.89	3.8	17.11 $\pm$.07	2.44 $\pm$.07	2.80 $\pm$.08	2.92 $\pm$.06	Howell
Mar 15.399	8.72	8.16	5.6	17.25	2.47 $\pm$.02	2.98 $\pm$.02	2.93 $\pm$.02	D & T*
Mar 17.281	8.72	8.19	5.7	17.28	2.59 $\pm$.02	2.97 $\pm$.03	2.95$\pm$.02	D & T

* D & T = Davies and Tholen (1996)

END