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Note

The surface composition of Ceres: Discovery of carbonates and iron-rich clays

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Abstract

We present observational evidence that carbonates and iron-rich clays are present on the surface of Ceres. These components are also present in CI chondrites and provide a means of explaining the unusual spectrum of this object as well as providing potential insight into its evolution.

Keywords: Asteroid Ceres; Asteroids, composition; Infrared observations; Spectroscopy

Ceres is the largest object in the main asteroid belt. Its spectrum in the visible and near-IR is typical of C-class asteroids and consistent with carbonaceous chondrites. It has an absorption band near 3 μm diagnostic of hydrated minerals, as detailed below. Ceres has been the subject of increased attention of late, with our knowledge of this body increasing rapidly since its identification as a target of NASA's Dawn spacecraft mission, and with its reclassification as a dwarf planet in 2006 by the International Astronomical Union (IAU). Thermodynamic modeling of Ceres' evolution (McCord and Sotin, 2005) and subsequent shape measurements using HST (Thomas et al., 2005; Erard et al., 2005) support the hypothesis that Ceres is differentiated and may have a subsurface ocean, reviewed by McCord et al. (2006). Consensus as to the exact surface composition of Ceres remains elusive, however. Work in the 1970s and 1980s concluded that Ceres was similar to carbonaceous chondritic meteorites largely based on overall characteristics such as albedo and spectral slope (Johnson and Fanale, 1973; McCord and Gaffey, 1974; Lebofsky et al., 1981; Larson et al., 1983; and others). McCord and Sotin (2005) provide an in-depth review of early spectroscopic work in the visible and near-infrared regions.

An absorption near 3 μm, diagnostic of hydrated or hydroxylated species on airless bodies, has been known on Ceres for nearly 30 years (Lebofsky, 1978; Jones et al., 1990; Rivkin et al., 2003), but there has been no agreement about the specific composition of the species responsible for the band on Ceres. Ceres' 3-μm band shape is unlike that of most C-class asteroids and is not known to occur in meteorites (Sato et al., 1997). This can be seen in Fig. 1, which shows a reflectance spectrum of the CM meteorite Murchison from the ASTER spectral library (http://speclib.jpl.nasa.gov) as well as new spectra of Ceres described below. The spectrum of Murchison is typical of most hydrated carbonaceous chondrites and most C-class asteroids with a 3-μm band (including 2 Pallas, for instance). Due to an additional absorption centered near 3.05 μm (first addressed by Lebofsky et al., 1981) and other apparent absorptions beyond that wavelength, Ceres does not exhibit the roughly linear rise beyond 2.9 μm seen in Murchison.

The first observations of the 3.05 μm band were interpreted as indicative of water ice frost (Lebofsky et al., 1981), which is only marginally stable on Ceres. Later work suggested ammoniated clays as a better fit (King et al., 1992), though such minerals have never been seen in meteorites. More recent observations have been interpreted as matching irradiated organic materials in the presence of ice (Vernazza et al., 2005). Most hydrated C-class asteroids are consistent with CM meteorites but, because some other asteroids have been found with Ceres-like band shapes (Rivkin et al., 2003), understanding the source of the 3-μm band has implications beyond Ceres.

To further study this problem, we obtained 2.2–4.0 μm spectroscopic observations of Ceres using the long-wavelength dispersed (LXD) mode of the SpeX instrument at the NASA Infrared Telescope Facility (IRTF) on Mauna Kea in Hawaii on May 17 and 18, 2005. The spectra are averages of more than 120 min of total integration time on May 17th and 80 min of integration time on May 18th. These data span a complete rotation of Ceres (9.075 h). Roughly an hour of integration time was obtained for each of two standard stars on each night. The data were reduced using Spextool software provided by the

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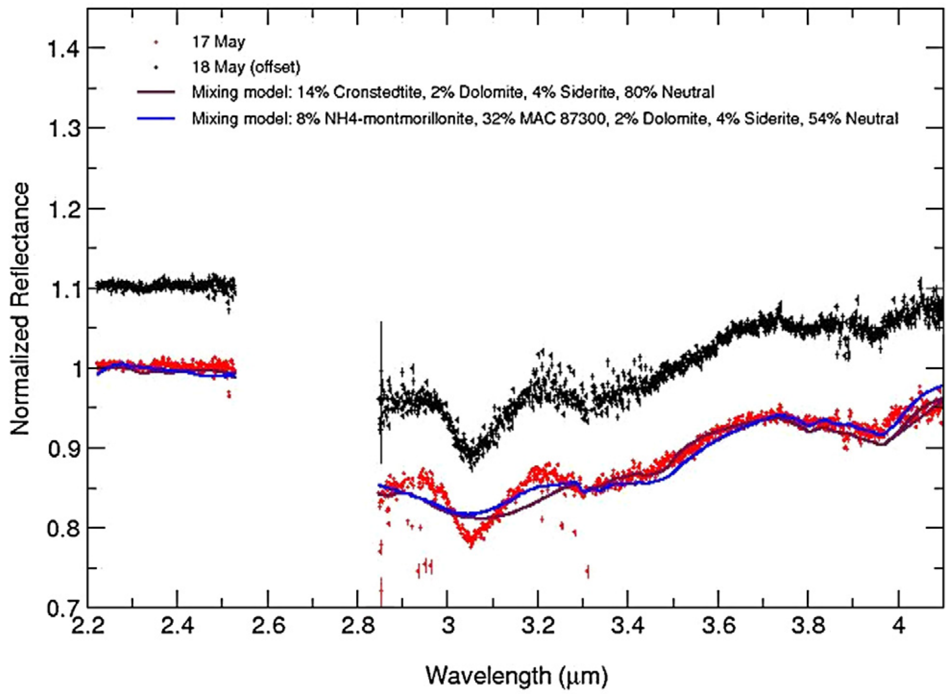
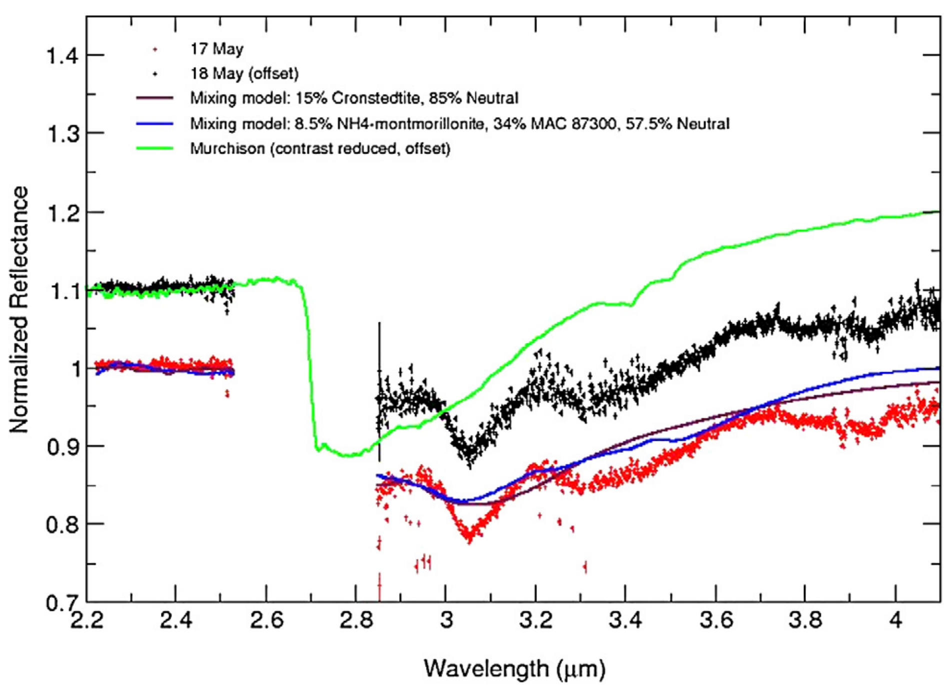


(a)



(b)

Fig. 1. 2.2–4.1 μm spectra of Ceres from 17 May and 18 May 2005, normalized to 1 at 2.2 μm. The 18 May spectrum (black) is offset from the 17 May spectrum for clarity. Also shown as solid lines are model spectra generated using a Hapke theory-based mixing model. These models use a carbonaceous chondrite, a neutral material, carbonates, and either an ammonium-bearing or iron-rich phyllosilicate as end-members. The top panel (a) shows the best-fit models using all of the components, indicating 6% carbonates. The bottom panel (b) removes the carbonates from the best-fit models, showing the requirement for carbonates in an acceptable fit. The bottom panel also shows the CM meteorite Murchison, showing the very different band shapes between it and Ceres. The end-member spectra were obtained from the RELAB and ASTER databases and contributed by Trude King. Data between 2.52 and 2.85 μm were omitted due to excessive spectral contamination from water in the Earth's atmosphere.

IRTF (Cushing et al., 2003). Following normal Spextool reduction procedures, the data were fit with an atmospheric model to remove residual telluric effects (similar to that done for shorter-wavelength data by Sunshine et al., 2004) and corrected for the influence of thermal flux (Rivkin et al., 2003).

Fig. 1 shows the reflectance spectra of Ceres at 2.2–4.0 μm from 17 and 18 May 2005. The gap in data from ∼2.55–2.85 μm is due to saturated water bands from the Earth's atmosphere. The Ceres spectra are offset from one another for clarity.

The broad 3-μm band in the Ceres spectra has several sub-bands, centered near 3.05, 3.3–3.4, and 3.8–3.9 μm. The 3.05-μm band has been attributed to a water ice frost, ammoniated phyllosilicates, and irradiated organic material, as mentioned above. Hydrated Fe-rich phyllosilicates can have band minima or shoulders near 3.05 μm, due to water chemically bound to iron or as the first overtone of the bending mode of water (Frost and Kloprogge, 2000; Frost et al., 2002). Hydrated Fe-rich phyllosilicates, such as cronstedtite, are known to occur in carbonaceous chondrites, and have spectra that are better matches to these meteorites in the visible and infrared (0.3–5 μm) than hydrated Mg-rich phyllosilicates (Calvin and King, 1997), although they have not been suggested as possible causes for the 3.05-μm band by previous workers. A band at 3.30 μm could possibly be due to aromatic hydrocarbons (Moroz et al., 1998) but can also be found in ammoniated phyllosilicates (Bishop et al., 2002), which could support the interpretation of King et al. (1992).

Anhydrous carbonates have absorption bands in the 3.3–3.4 and 3.8–3.9 μm regions (Calvin et al., 1994; Bishop et al., 1998), matching the bands seen in the Ceres spectrum. Though much weaker, absorption bands are also present in carbonate spectra near 2.3 μm. Those wavelengths are in an overlap region between orders in the LXD data for Ceres, which makes interpretation of that spectral region problematic in the telescopic data. There is some structure at those wavelengths that is consistent with carbonates, but it is not conclusive in these data since the joining of the two orders is not necessarily perfect.

We used a Hapke bi-directional scattering model to mix end-member mineral spectra to simulate our whole-disk observations of Ceres. Using software developed for analysis of NEAR Shoemaker spectra of asteroid 433 Eros (Clark et al., 2002, 2004), we simulated intimate mixtures of a set of 6 end-member spectra. Our end-members were: the carbonaceous chondrite MAC 87300, an ammonium-bearing montmorillonite or an iron-rich phyllosilicate (cronstedtite), three different carbonates [siderite ($FeCO_3$), calcite ($CaCO_3$), and dolomite ($CaMgCO_3$)], and a neutral phase spectrum with an albedo of 10%. Spectrally dark and neutral phases have been necessary in all spectral modeling of airless rocky planetary surfaces to represent low-albedo and/or noncrystalline components. End-member spectra were obtained from the RELAB and ASTER spectral libraries, except for the ammonium-bearing montmorillonite spectrum (T. King, personal communication). All end-members were measured at fine (<45 μm) grain sizes. Before searching for a best fit over a grid of end-member mixtures, our spectra and our models were normalized to 1 at 2.2 μm. This means that albedo information (often used as a constraint in scattering models) is not used. Our mixture model simulations are not meant to indicate unique determinations of composition. However, if the assumption is made that the end-member choices are accurate, such models can be used as indicators of relative proportions of detected components.

Best fit mixture model spectra (Fig. 1) are dominated by the neutral material (50–80%) and are consistent with a 4–6% contribution from carbonates regardless of whether an iron-rich or ammonium-bearing clay is used. These results are comparable to proportions found in CI meteorites (average of ∼5%; Endress et al., 1996), and are higher than those found in the CM meteorites (∼2%; Benedix et al., 2003). The models preferred dolomite and siderite to calcite, but we are not willing to conclude that calcite is excluded based only on these models. Although albedo is not constrained during fitting, the model spectra have albedos consistent with measurements of Ceres (0.08 for the NH4-montmorillonite model, 0.12 for the Fe-clay model, and 0.09 measured for Ceres). The LXD data were consistent with both iron-rich and ammonium-bearing clays, though the two models result in slightly different band centers. In both models, however, the 3.05 μm band is wider than is observed on Ceres. Since our models do not currently account for the effects of temperature differences between laboratory and space conditions on spectra, it is possible that temperature is part of the cause of the discrepancy (Singer and Roush, 1985). A grain size difference between the end-member samples and Ceres' surface is another possible cause of the difference. Further exploring these possibilities are beyond the scope of this work.

An emissivity spectrum of Ceres obtained from the Kuiper Airborne Observatory (KAO) (digitized from Cohen et al., 1998) shows emission features near 7, 9.5, and 11.5 μm (Fig. 2). We performed spectrum library searches and visual

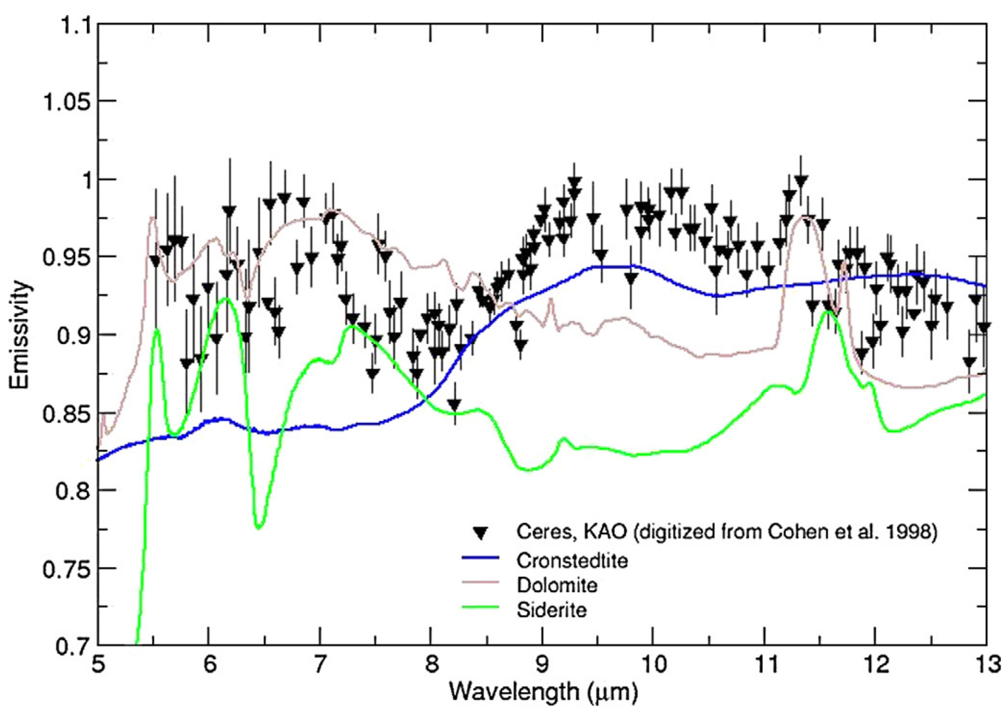


Fig. 2. 5–13 μm emissivity spectrum of Ceres obtained using the Kuiper Airborne Observatory (KAO), published by Cohen et al. (1998). Previous attempts to match the mid-infrared spectrum of Ceres to carbonaceous chondrites, ammonium-bearing, or magnesium-rich phyllosilicates by earlier authors were unsuccessful. Here, dolomite and siderite (gray and green, respectively) are compared to Ceres (black points), as well as the iron-rich clay cronstedtite (blue). Because current scattering models are unlikely to be valid at these wavelengths for the particle sizes expected on Ceres, we can only present a qualitative comparison. Nevertheless, the emissivity features between 5–7 and 11.2 μm appear consistent with carbonates, and the emissivity peak near 9.5–10 μm is consistent with cronstedtite. Because we find ammonium-bearing clays to be inconsistent with this wavelength region, we prefer an interpretation of iron-bearing clays as the cause of the 3-μm band. The end-member spectra were obtained from the RELAB and ASTER databases and converted to emissivity using Kirchhoff's Law.

comparisons to aid in interpretation of the spectral features in the KAO spectrum. Included in Fig. 2 are cronstedtite and dolomite (reflectance spectra converted to emissivity using Kirchhoff's Law). These two minerals, not previously considered by Cohen et al. (1998), do an excellent job of matching the peaks seen in Ceres' mid-IR spectrum: the 9.5 µm peak is well matched by the cronstedtite spectrum and the remaining peaks are well matched by the carbonates. Carbonaceous chondrites have absorption bands near 6.8 µm that have been attributed to carbonates (Miyamoto, 1987), and Calvin and King found that iron-rich clays were a good match to CM chondrite spectra in the mid-IR (though interestingly, magnesium-rich clays matched their CI spectrum better in this wavelength range). We find, as did Cohen et al., that ammoniated saponite spectra are also not consistent with Ceres' spectrum in the mid-IR. Lizardite (a Mg-rich phyllosilicate not shown) also fails to match the 9.5 µm peak. We note that additional spectra of Ceres in this wavelength region (Dotto et al., 2000; Lim et al., 2005) are not as suggestive as our data of the presence of cronstedtite. However, magnesium-rich and ammonium-bearing clays are also not suggested by those spectra. While the spectrum of Ceres in the 3-µm region alone does not lead us to prefer either of Fe-rich or ammonium-rich hydrated phyllosilicates over the other, the mid-IR KAO spectrum clearly suggests the former as a better match. Therefore, considering the spectrum of Ceres as a whole, we prefer Fe-rich phyllosilicates over other candidate materials for the 3.05 µm band.

Ceres represents only the third Solar System object suggested to have carbonates, along with Earth and Mars. Carbonates have been seen in protostellar dust shells and have been interpreted as having formed through gas phase interactions with grains or by condensing directly from the solar nebula rather than through aqueous alteration (Kemper et al., 2002). In meteorites, they are thought to be the products of aqueous alteration. McCord and Sotin (2005) considered the chemical evolution of Ceres undergoing aqueous alteration and concluded that CO_2 could have been formed and released. Carbonates would easily form in such a scenario.

Tomeoka and Buseck (1985) outlined a multi-step aqueous alteration sequence for carbonaceous chondrites. Cronstedtite is the dominant alteration product partway through the sequence, which continues on to make more magnesium-rich phyllosilicates as the iron enters magnetite. Further laboratory studies also found cronstedtite to be more indicative of earlier rather than later stages of alteration (Browning et al., 1996). If Ceres is dominated by iron-rich rather than magnesium-rich clays, and if there really is, or was, a subsurface ocean, the implication is that the surface of Ceres did not experience aqueous alteration to completion, despite the apparent availability of large amounts of water, and that its surface had limited exchange with the interior. This is consistent with the modeling of McCord and Sotin (2005) which predicts ice in the outer 10 km of Ceres would remain frozen, although they note that the frozen crust would be gravitationally unstable and likely overturn, melt, and refreeze. A more detailed consideration of aqueous alteration in the outermost portion of Ceres' crust is beyond the scope of this work.

Rosenberg et al. (2001) modeled aqueous alteration in CM chondrites and found that cronstedtite forms when precursor material was oxidized rather than reduced. As briefly addressed above, there are two different 3 µm band shapes found on asteroids, one group with band shapes like Ceres, the other similar to 2 Pallas and the CM meteorites (Rivkin et al., 2003). If the two different band shapes at 3 µm are caused by differing abundances of hydrated iron-rich pyllosilicates, then it is possible that this band shape could be used as a proxy for the oxidation state of the asteroid belt and, by inference, the solar nebula.

Conclusions

New observations of Ceres in the 2–4 µm spectral region were obtained in May 2005 using SpeX on the IRTF. Analysis of thermally-corrected spectra indicates the presence of carbonates at an abundance of 4–6% on Ceres' surface, similar to what is seen in CI meteorites. These carbonates are responsible for bands in the 3.3 and 3.8–3.9 µm region. Iron-rich phyllosilicates or ammonium-bearing phyllosilicates can both account for an absorption band at 3.05 µm, but consideration of mid-IR data from Cohen et al. (1998) leads us to favor iron-rich phyllosilicates. Such minerals, including cronstedtite, are commonly found in carbonaceous chondrites and suggest relatively oxidized precursors and aqueous alteration that did not go to completion.

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References

Benedix, G.K., Leshin, L.A., Farquhar, J., Jackson, T., Theimens, M.H., 2003. Carbonates in CM2 chondrites: Constraints on alteration conditions from oxygen isotopic compositions and petrographic observations. Geochim. Cosmochim. Acta 67, 1577–1588.

Bishop, J.L., Pieters, C.M., Hiroi, T., Mustard, J.F., 1998. Recognition of minor constituents in reflectance spectra of ALH 84001 chips and the importance for remote sensing on Mars. Meteorit. Planet. Sci. 33, 693–698.

Bishop, J.L., Banin, A., Mancinelli, R.L., Klovstad, M.R., 2002. Detection of soluble and fixed NH_4^+ in clay minerals by DTA and IR reflectance spectroscopy: A potential tool for planetary surface exploration. Planet. Space Sci. 50, 11–19.

Browning, L.B., Mcsween Jr., H.Y., Zolensky, M.E., 1996. Correlated alteration effects in CM carbonaceous chondrites. Geochim. Cosmochim. Acta 60, 2621–2633.

Calvin, W.M., King, T.V.V., 1997. Spectral characteristics of iron-bearing phyllosilicates: Comparison to Orgueil (CI1), Murchison and Murray (CM2). Meteorit. Planet. Sci. 32, 693–701.

Calvin, W.M., King, T.V.V., Clark, R.N., 1994. Hydrous carbonates on Mars? Evidence from Mariner 6/7 infrared spectrometer and ground-based telescopic spectra. J. Geophys. Res. 99, 14659–14675.

Clark, B.E., Helfenstein, P., Bell, J.F., Peterson, C., Veverka, J., Izenberg, N.I., Domingue, D., Wellnitz, D., McFadden, L., 2002. NEAR infrared spectrometer photometry of Asteroid 433 Eros. Icarus 155, 189–204.

Clark, B.E., Bus, S.J., Rivkin, A.S., McConnochie, T., Sanders, J., Shah, S., Hiroi, T., Shepard, M., 2004. E-type asteroid spectroscopy and compositional modelling. J. Geophys. Res. 109, doi:10.1029/2003JE002200.

Cohen, M., Witteborn, F.C., Roush, T., Bregman, J., Wooden, D., 1998. Spectral irradiance calibration in the infrared. VIII. 5–14 micron spectroscopy of the Asteroids Ceres, Vesta, and Pallas. Astron. J. 115, 1671–1679.

Cushing, M.C., Vacca, W.D., Rayner, J.T., 2003. Spextool: A Spectral Extraction Package for SpeX, a 0.8–5.5 micron Cross-Dispersed Spectrograph. Publ. Astron. Soc. Pacific 115, 383–388.

Dotto, E., and 10 colleagues, 2000. ISO results on bright main belt asteroids: PHT-S observations. Astron. Astrophys. 358, 1133–1141.

Endress, M., Zinner, E., Bischoff, A., 1996. Early aqueous activity on primitive meteorite parent bodies. Nature 379, 701–703.

Erard, S., Forni, O., Ollivier, M., Dotto, E., Roush, T., Poulet, F., Müller, T., 2005. The 2004 opposition of Ceres observed with adaptive optics on the VLT. Lunar Planet. Sci. XXXVI. Abstract 1388.

Frost, R.L., Kloprogge, J.T., 2000. Vibrational spectroscopy of ferruginous smectite and nontronite. Spectrochim. Acta A 56, 2177–2189.

Frost, R.L., Kloprogge, J.T., Ding, Z., 2002. The Garfield and Uley nontronites—An infrared spectroscopic comparison. Spectrochim. Acta A 58, 1881–1894.

Johnson, T.V., Fanale, F.P., 1973. Optical properties of carbonaceous chondrites and their relationship to asteroids. J. Geophys. Res. 78, 8507–8518.

Jones, T.D., Lebofsky, L.A., Lewis, J., Marley, M.S., 1990. The composition and origin of the C, P, and D asteroids: Water as a tracer of thermal evolution in the outer belt. Icarus 88, 172–192.

Kemper, F., Jäger, C., Waters, L.B.F.M., Henning, Th., Molster, F.J., Barlow, M.J., Lim, T., de Koter, A., 2002. Detection of carbonates in dust shells around evolved stars. Nature 415, 295–297.

King, T.V.V., Clark, R.N., Calvin, W.M., Sherman, D.M., Brown, R.H., 1992. Evidence for ammonium-bearing minerals on Ceres. Science 255, 1551–1553.

Larson, H.P., Feierberg, M.A., Lebofsky, L.A., 1983. The composition of 2 Pallas and its relation to primitive meteorites. Icarus 56, 398–408.

Lebofsky, L.A., 1978. Asteroid 1 Ceres: Evidence for water of hydration. Mon. Not. R. Astron. Soc. 182, 17–21.

Lebofsky, L.A., Feierberg, M.A., Larson, H.P., Tokunaga, A.T., 1981. The 1.7- to 4.2-micron spectrum of Asteroid 1 Ceres—Evidence for structural water in clay minerals. Icarus 48, 453–459.

Lim, L.F., McConnochie, T.H., Bell III, J.F., Hayward, T.L., 2005. Thermal infrared (8–13 μm) spectra of 29 asteroids: The Cornell Mid-Infrared Asteroid Spectroscopy (MIDAS) survey. Icarus 173, 385–408.

McCord, T.B., Gaffey, M.J., 1974. Asteroids: Surface composition from reflection spectroscopy. Science 186, 352–355.

McCord, T.B., Sotin, C., 2005. Ceres: Evolution and current state. J. Geophys. Res. 110, doi:10.1029/2004JE002244.

McCord, T.B., McFadden, L.A., Russell, C.T., Sotin, C., Thomas, P.C., 2006. Ceres, Vesta, and Pallas: Protoplanets, not asteroids. EOS Trans. Am. Geophys. Union 878, 105–109.

Miyamoto, M., 1987. Infrared diffuse reflectances (2.5–25 μm) of some meteorites. Icarus 70, 146–152.

Moroz, L.V., Arnold, G., Korochantsev, A.V., Wasch, R., 1998. Natural solid bitumens as possible analogs for cometary and asteroid organics. Icarus 134, 253–268.

Rivkin, A.S., Davies, J.K., Johnson, J.R., Ellison, S.L., Trilling, D.E., Brown, R.H., Lebofsky, L.A., 2003. Hydrogen concentrations on C-class asteroids derived from remote sensing. Meteorit. Planet. Sci. 38, 1383–1398.

Rosenberg, N.D., Browning, L., Bourcier, W.L., 2001. Modeling aqueous alteration of CM carbonaceous chondrites. Meteorit. Planet. Sci. 36, 239–244.

Sato, K., Miyamoto, M., Zolensky, M.E., 1997. Absorption bands near three micrometers in diffuse reflectance spectra of carbonaceous chondrites: Comparison with asteroids. Meteoritics 32, 503–507.

Singer, R.B., Roush, T.L., 1985. Effects of temperature on remotely sensed mineral absorption features. J. Geophys. Res. 90, 12434–12444.

Sunshine, J.M., Bus, S.J., McCoy, T.J., Burbine, T.H., Corrigan, C.M., Binzel, R.P., 2004. High-calcium pyroxene as an indicator of igneous differentiation in asteroids and meteorites. Meteorit. Planet. Sci. 39, 1343–1357.

Thomas, P.C., Parker, J.W., McFadden, L.A., Russell, C.T., Stern, S.A., Sykes, M.V., Young, E.F., 2005. Differentiation of the Asteroid Ceres as revealed by its shape. Nature 437, 224.

Tomeoka, K., Buseck, P.R., 1985. Indicators of aqueous alteration in CM carbonaceous chondrites: Microtextures of a layered mineral containing Fe, S, O and Ni. Geochim. Cosmochim. Acta 49, 2149–2163.

Vernazza, P., Mothé-Diniz, T., Barucci, M.A., Birlan, M., Carvano, J.M., Strazzulla, G., Fulchignoni, M., Migliorini, A., 2005. Analysis of near-IR spectra of 1 Ceres and 4 Vesta, targets of the Dawn mission. Astron. Astrophys. 436, 1113–1121.