

Ammoniated phyllosilicates with a likely outer Solar System origin on (1) Ceres

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Studies of the dwarf planet (1) Ceres using ground-based and orbiting telescopes have concluded that its closest meteoritic analogues are the volatile-rich CI and CM carbonaceous chondrites^{1,2}. Water in clay minerals³, ammoniated phyllosilicates⁴, or a mixture of Mg(OH)₂ (brucite), Mg₂CO₃ and iron-rich serpentine^{5,6} have all been proposed to exist on the surface. In particular, brucite has been suggested from analysis of the mid-infrared spectrum of Ceres⁶. But the lack of spectral data across telluric absorption bands in the wavelength region 2.5 to 2.9 micrometres—where the OH stretching vibration and the H₂O bending overtone are found—has precluded definitive identifications. In addition, water vapour around Ceres has recently been reported⁷, possibly originating from localized sources. Here we report spectra of Ceres from 0.4 to 5 micrometres acquired at distances from ~82,000 to 4,300 kilometres from the surface. Our measurements indicate widespread ammoniated phyllosilicates across the surface, but no detectable water ice. Ammonia, accreted either as organic matter or as ice, may have reacted with phyllosilicates on Ceres during differentiation. This suggests that material from the outer Solar System was incorporated into Ceres, either during its formation at great heliocentric distance or by incorporation of material transported into the main asteroid belt.

The Visible-Infrared Mapping Spectrometer VIR⁸ on the Dawn spacecraft⁹ obtained multi-spectral images of Ceres' surface in the spectral range 0.4–5 μm with an instantaneous field of view of 250 μrad (Fig. 1). This range includes the 2.6–2.9 μm spectral region precluded

from telescopic measurements owing to the atmospheric absorptions. As such, Dawn data provide new constraints on Ceres' surface composition.

The average spectrum of Ceres' surface measured by VIR shows a low level of reflectance combined with prominent thermal emission at longer wavelengths, indicative of a very dark, warm surface. At the spatial scale of ~11 km per pixel, daytime surface temperatures of Ceres span the range 180–240 K at a heliocentric distance of 2.86 AU, with maximum temperatures inferred in the equatorial region, corresponding to the minimum solar incidence angle. This range of temperatures is generally incompatible with a widespread occurrence of water ice on the surface, even if very small localized occurrences of water ice cannot be excluded¹⁰.

The geometric albedo obtained from VIR is 0.088 ± 0.006 at 0.55 μm, derived from Hapke modelling of the average surface photometric properties of the body¹¹. The measured value of the albedo agrees with Hubble Space Telescope observations in the F555W filter¹². Given the low albedo of the surface, single scattering dominates the reflectance. The thermally corrected reflectance spectrum of Ceres (Fig. 1b) shows that the 2.6–4.2 μm wavelength region is characterized by a broad asymmetric feature, characteristic of H₂O/OH bearing materials. Within this broad absorption are several distinct absorption bands at 2.72 μm, 3.05–3.1 μm, 3.3–3.5 μm and 3.95 μm.

Laboratory spectra of CM and CI carbonaceous chondrites measured under anhydrous conditions¹³ show the same prominent 2.7 μm OH absorption band as the Ceres spectrum, suggesting

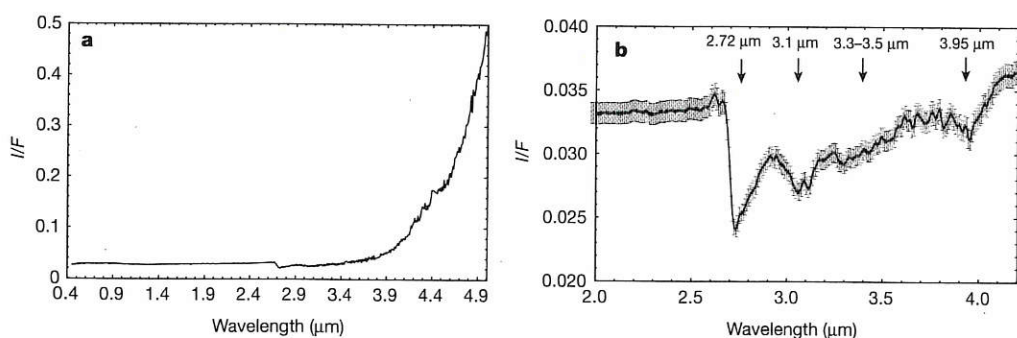


Figure 1 | Average spectrum of Ceres. a, Average spectrum of Ceres from 0.4 μm to 5 μm. No smoothing has been applied to the spectrum and some instrument artefacts are still present, especially in the thermal range (4.2–4.6 μm). Error bars were calculated taking into account a mean absolute deviation of the calibration uncertainties along the 256 samples,

but are not shown for clarity; they are of the same order as those in b. b, Expanded thermal-removed average Ceres spectrum in the 2–4.2 μm range. Main bands are indicated by arrows. *I/F* is the spectral radiance divided by the solar spectral irradiance.

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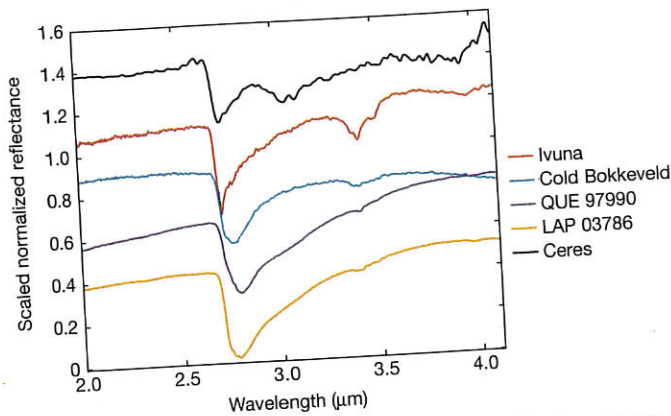


Figure 2 | Spectrum of Ceres compared with spectra of carbonaceous chondrites. Shown are normalized reflectance spectra of CM/CI carbonaceous chondrites (Ivuna, Cold Bokkeveld, QUE 97990 and LAP 03786) measured under dry conditions¹³ compared with Ceres' spectrum acquired by VIR. The spectra have been offset for clarity. We thank D. Takir for the spectra of carbonaceous chondrites.

some mineralogical similarity, consistent with the idea that these materials are relevant meteoritic analogues for Ceres^{1,2}. However, these chondrites are not a good match with Ceres at other wavelengths (Fig. 2). Even if the spectrum of Ceres is broadly similar to that of CM chondrites, distinct spectral features indicate variations in mineral proportions that may reflect differences in alteration pathways and/or formation conditions. For instance, the $\sim 4.0 \mu\text{m}$ absorption is stronger in the Ceres spectrum than in most CM/CI spectra, whereas the $\sim 3.4 \mu\text{m}$ feature is usually stronger in CM/CIs. Moreover, CM and CI chondrites lack Ceres' distinctive signature at $3.05\text{--}3.1 \mu\text{m}$.

The $3.05\text{--}3.1 \mu\text{m}$ band dominates Ceres' ground-based spectra, and was also observed on two other asteroids¹⁴. This signature has been attributed to a variety of different phases including water ice, hydrated or NH_4 -bearing clays and brucite³⁻⁶ (Extended Data Fig. 1). Brucite, in particular, clearly shows this narrow characteristic absorption¹⁵. Ammoniated mineral species, including NH_4 -bearing annite and NH_4 -montmorillonite, have an absorption feature near $3.06 \mu\text{m}$, which could account for this band.

VIR observations show a strong and narrow absorption centred at $2.72\text{--}2.73 \mu\text{m}$. This characteristic feature is distinctive for OH-bearing minerals (Extended Data Fig. 1). H_2O -bearing phases, however, show a much broader absorption band that is a poor match for the Ceres spectrum. Water ice does not fit the observed spectrum, consistent with its instability at the maximum surface temperature. OH stretching vibrations occur in the $2.7\text{--}2.85 \mu\text{m}$ range for phyllosilicates¹⁶, with band centres at different wavelengths for different species.

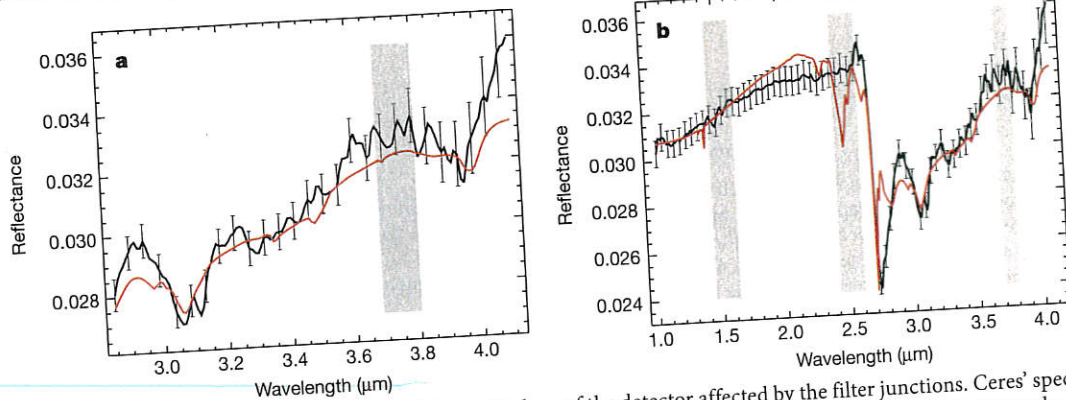


Figure 3 | Spectral fits of the spectrum of Ceres. a, Results of the spectral fitting model (red curve) using brucite, Mg-carbonate, dark component and cronstedtite⁶; b, the same model (red curve) is shown over an extended spectral range ($1\text{--}4.2 \mu\text{m}$). Vertical grey bars represent regions

Ceres is rich in absorption bands in the $3\text{--}4 \mu\text{m}$ region, but the spectral range $1.0\text{--}2.5 \mu\text{m}$ lacks distinctive features. Conversely, some terrestrial H_2O - and OH-bearing phases show numerous diagnostic bands over this spectral range. For example, brucite has a prominent $2.46 \mu\text{m}$ band that is absent in the Ceres spectra (Extended Data Fig. 1). Also, the vibrations due to the OH overtone at about $1.4 \mu\text{m}$ and the bands due to H-O-H combination stretching and bending vibrations in the $1.9 \mu\text{m}$ region are absent in the Ceres spectrum. The combination of phyllosilicates with other species, however, can mask the presence of such bands.

In order to model Ceres' surface spectrum, we solved the radiative transfer equation in a particulate medium, using the Hapke model¹⁷. We investigated several different combinations of mineralogical phases (Methods and Extended Data Tables 1 and 2). We started with a simple combination of water ice with a dark component (amorphous carbon or magnetite), but the presence of ice gives rise to clear absorption bands at $1.5 \mu\text{m}$ and $2 \mu\text{m}$ that are not present in our data (Extended Data Fig. 2). Also, the $3 \mu\text{m}$ ice band centre does not fit the Ceres data. Magnetite (or carbon) in the fits represents a highly absorbing species whose specific character is not defined in this analysis. However, the mixture with magnetite fits the spectral slope between $1 \mu\text{m}$ and $2.6 \mu\text{m}$ better. For this reason we choose to use magnetite in the other mixtures.

While the mixture of brucite, MgCO_3 , a dark component, and Fe-serpentine (cronstedtite)⁶ is able to match the Ceres spectrum in the $2.9\text{--}4.2 \mu\text{m}$ range, it fails to fit the intense $2.7 \mu\text{m}$ band (Fig. 3). Also, mixtures of water ice with CM or CI carbonaceous chondrite do not fit the Ceres spectrum (Extended Data Fig. 3 and Extended Data Table 2). The fit is also poor in the case of adding brucite and water to carbonaceous chondrites (Extended Data Fig. 3 and Extended Data Table 2). The prominent $2.7 \mu\text{m}$ band can be fitted by a mixture of phyllosilicates such as Mg-serpentine (antigorite) or tochilinite (structurally interlayered brucite and iron sulphide), with Fe-serpentine (cronstedtite), carbonate (dolomite) and magnetite (Extended Data Fig. 4a, b). The fit with antigorite is slightly better in reproducing the depth and centre of the $2.7 \mu\text{m}$ band; thus for the following fits we use antigorite to reproduce the $2.7 \mu\text{m}$ feature. However, the fit does not fully reproduce the absorption at $3.05\text{--}3.1 \mu\text{m}$. By analogy with CM chondrites, however, tochilinite is more likely than antigorite to be in equilibrium with cronstedtite and thus may be a more plausible phase¹⁸. Addition of brucite to the mixture of phyllosilicates, carbonates and magnetite described above slightly improves the fits at $3.05\text{--}3.1 \mu\text{m}$, but the fits are not satisfactory at shorter wavelengths (Extended Data Fig. 4c, d and Extended Data Table 2).

Other species that have clear absorptions at $3.05\text{--}3.1 \mu\text{m}$ are ammoniated-bearing minerals, which also show absorptions at $3.3 \mu\text{m}$ (ref. 19). The best fit of Ceres' spectrum over the infrared range is consistently obtained by adding ammoniated phyllosilicates to a dark material

of the detector affected by the filter junctions. Ceres' spectrum is in black. Error bars are calculated taking into account a mean absolute deviation of the calibration uncertainties along the 256 samples.

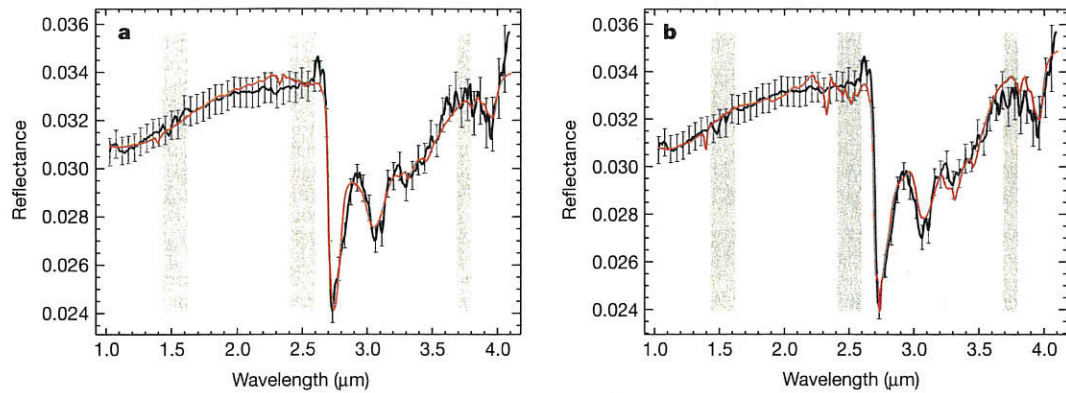


Figure 4 | Spectral fits of the spectrum of Ceres with ammonia-bearing species. **a**, Results of the spectral fitting model (red curve) using NH_4 -montmorillonite, antigorite, Mg-carbonate, and dark component;

(magnetite), antigorite and carbonate (Fig. 4). Mixtures with different ammoniated clays (Fig. 4) can match the Ceres spectrum, but the specific clay mineral cannot be determined. Carbonates are always needed in the fit but the specific carbonate mineral is not fully constrained because dolomite, magnesite and calcite produce equivalent matches to the observed Ceres spectrum (Extended Data Fig. 5 and Extended Data Table 2).

Ammoniated clays on Ceres have been suggested previously⁴, possibly formed by reaction with ammonia ice. Recent observation of substantial amounts of ammonia contained in organic compounds in some CI, CM and CR chondrites²⁰ suggests another mechanism for the formation of ammoniated clays on Ceres. The consistent ¹⁵N-enrichment of carbonaceous chondrite organic matter may indicate that enrichment occurred in the solar nebula before star formation²⁰, although ammonia was also likely to have been processed into more complex molecules in the protoplanetary disk and parent bodies. Modest heating to 300–400 °C of NH_4 -bearing organic matter in carbonaceous chondrites releases ammonia²⁰, and a similar process on Ceres could have plausibly produced ammoniated phyllosilicates. The ability of smectite, especially montmorillonite, to incorporate ammonia by cation exchange is well documented²¹.

Ceres' surface enrichment in ammoniated phyllosilicates and relatively low bulk density pose significant challenges to understanding its origin and formation. One view holds that Ceres and most C-type asteroids could have formed close to their current locations, inferred to be near the water snow line²². However, CI/CM meteorites have bulk water contents of 15%–20% at most, whereas Ceres is inferred to be ~30% water by mass, on the basis of its bulk density. This may indicate that Ceres retained more volatiles than objects represented in the meteorite collection, or that it accreted from more volatile-rich material.

We have shown here that the altered CM and CI carbonaceous chondrites do not offer a good spectral match for Ceres, nor do all carbonaceous chondrites show evidence of exposure to significant amounts of ammonia. Therefore, it seems unlikely that a substantial population of ammonia-rich planetesimals could have formed locally at Ceres' current location in the main belt, even if the water snow line episodically migrated about 1 AU during the evolution of the protoplanetary disk^{22–24}. However, it is possible that Ceres grew close to its present position by accreting pebble-sized objects, some of which could have drifted inward from larger heliocentric distances²⁵ where ammonia was stable. If the source of NH_3 for ammoniated phyllosilicate was ammonia-bearing organic matter, Ceres could have accreted organics originally formed by irradiation of N_2 ices condensed near or beyond the orbit of Neptune.

Alternatively, Ceres may itself have formed further out in the Solar System, presumably in the trans-Neptunian disk, before being subsequently implanted in the main belt²⁶. This view is corroborated by the presence of ammonia ice on other large trans-Neptunian objects, such

as Orcus and Charon^{27,28}. The implantation of Ceres in the main belt could have taken place during a migratory phase of the giant planets, either during their growth in the protoplanetary disk²⁹, or at a later time as a result of an orbital instability³⁰.

Online Content Methods, along with any additional Extended Data display items and Source Data, are available in the online version of the paper; references unique to these sections appear only in the online paper.

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Author Information The VIR calibrated data will be made available through the PDS Small Bodies Node website (<http://sbn.pds.nasa.gov/>). Reprints and permissions information is available at www.nature.com/reprints. The authors declare no competing financial interests. Readers are welcome to comment on the online version of the paper. Correspondence and requests for materials should be addressed to M.C.D.S. (maria Cristina.desanctis@iaps.inaf.it).