Brucite and carbonate assemblages from altered olivine-rich materials on Ceres

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The dwarf planet Ceres is the largest object in the asteroid belt, and is generally thought to be a differentiated body composed primarily of silicate materials and water ice[1,2]. Some remotely observed features, however, indicate that Ceres may instead have a composition more similar to that of the most common types of carbonaceous meteorite[3-7]. In particular, Ceres has been shown to have a distinct infrared absorption feature centred at a wavelength of ~3.06 μm that is superimposed on a broader absorption from ~2.8 to 3.7 μm (refs 5, 8), which suggests the presence of OH- or H_2O-bearing phases. The specific mineral composition of Ceres and its relationship to known meteorite mineral assemblages, however, remains uncertain. Here we show that the spectral features of Ceres can be attributed to the presence of the hydroxide brucite, magnesium carbonates and serpentines, a mineralogy consistent with the aqueous alteration of olivine-rich materials. We therefore suggest that the thermal and aqueous alteration history of Ceres is different from that recorded by carbonaceous meteorites, and that samples from Ceres are not represented in existing meteorite collections.

The potential relationship between Ceres and carbonaceous chondrites has been based largely on qualitative similarities in the spectral properties of these materials, including the presence of hydrated phases on Ceres as demonstrated by absorptions in the 3 μm region as well as a relatively low albedo. Both of these spectral properties are grossly similar to the C1 and C2 carbonaceous chondrites[9], but the shape of Ceres' 3 μm feature, including an intriguing absorption at 3.06 μm, is distinct from spectra of the C1 and C2 chondrites.

The absorption feature at 3.06 μm in Ceres' reflectance spectrum has been attributed to a variety of phases over the past 30 years, including an initial interpretation of water ice[5,10]. Although it has been shown that water ice may be stable in the upper metre of the surface, it is not stable at the optical surface, making this an unsuitable candidate[11]. Later studies suggested the feature was caused by the presence of hydrated smectite clays[6] or NH_4-bearing smectites[12]. Smectite clays have been observed in carbonaceous chondrites, but they do not have absorption features at 3.06 μm, even when dehydrated, and readily lose their interlayer H_2O under low relative humidity or vacuum. In contrast, NH_4-bearing smectites do have an absorption at 3.06 μm (ref. 12), but they have extra absorptions in the 3 μm region that are not observed in Ceres' spectrum and they have not been detected in chondritic meteorites. More recently it was suggested that the 3 μm region could be modelled by the presence of carbonates and the Fe-rich serpentine cronstedtite[7]. Cronstedtite is a known constituent of the carbonaceous chondrite matrix[13–15], but its spectrum does not have a feature at 3.06 μm even when heated to remove any potential surface-adsorbed H_2O (see Supplementary Information), which

produces relatively poor fits in this wavelength range[7]. The result from these studies is that there is no clear consensus on the origin of this spectral feature, the composition of hydrous phase(s) on Ceres and the genetic relationship, if one exists, between Ceres and the carbonaceous chondrites.

A thermally corrected reflectance spectrum of Ceres[7] shows that the 2.8–4.2 μm wavelength region is characterized by distinct absorptions at 3.06, 3.3, 3.44, 3.8 and 3.94 μm, all superposed on a broad 'hydration' feature that spans these wavelengths (Fig. 1). The narrow absorption feature centred at 3.06 μm is distinctive for hydrated minerals and is not present in serpentines, sulphates, carbonates and non-ammoniated smectites, even though all have been detected in carbonaceous chondrites. The only common hydrated alteration product of mafic minerals that shows this relatively narrow absorption is brucite, $Mg(OH)_2$ (Fig. 1). The 3.06 μm absorption in brucite is one of several OH stretching vibrations in the 2–4 μm region[16]. Although pure brucite is not a major component of meteorites, brucite-like layers occur in the matrix of C2 chondrites in the form of tochilinite, a mineral that consists of interlayered sulphide and brucite sheets[14,17,18]. However, the spectrum of tochilinite is distinct from pure brucite and lacks a 3.06 μm absorption[19]. We conclude that the 3.06 μm feature of Ceres can be explained by the presence of brucite and does not require the presence of smectite clays[6], ammoniated clays[12] or water ice[10].

In addition to brucite, absorptions at ~3.3, 3.44, 3.8 and 3.94 μm are consistent with the presence of carbonates[7]. We have used a simple numerical linear mixing model based on laboratory reflectance spectra to qualitatively test how well mixtures of these and other components can fit the observed Ceres spectrum (see the Methods section and Supplementary Information). The linear mixing model reveals that all of the major spectral features from ~3.0–4.2 μm can be explained by the presence of brucite, Mg carbonates and dark components (Fig. 1). The fit is improved from 2.85–3.0 μm when cronstedtite is included in the model, but other phases with broad OH bands at this wavelength could produce a similar effect. These results demonstrate that the reflectance spectrum of Ceres can be fitted remarkably well in the 3 μm region with a minimum of three components and that only OH-bearing phases are required; there is no clear evidence for H_2O at the optical surface. The Mg-bearing carbonates dolomite and magnesite yield better fits than calcite or siderite. This result is consistent with the types of carbonate detected in C1 chondrites as well as the types of carbonate produced from the alteration of brucite in the presence of CO_2-rich fluids[20,21].

Emissivity data of Ceres over the ~5–13 μm wavelength range[7,22] can also be used to constrain the surface composition and for comparison with the near-infrared results. The emissivity data[22] were converted to reflectance and modelled as linear mixtures of
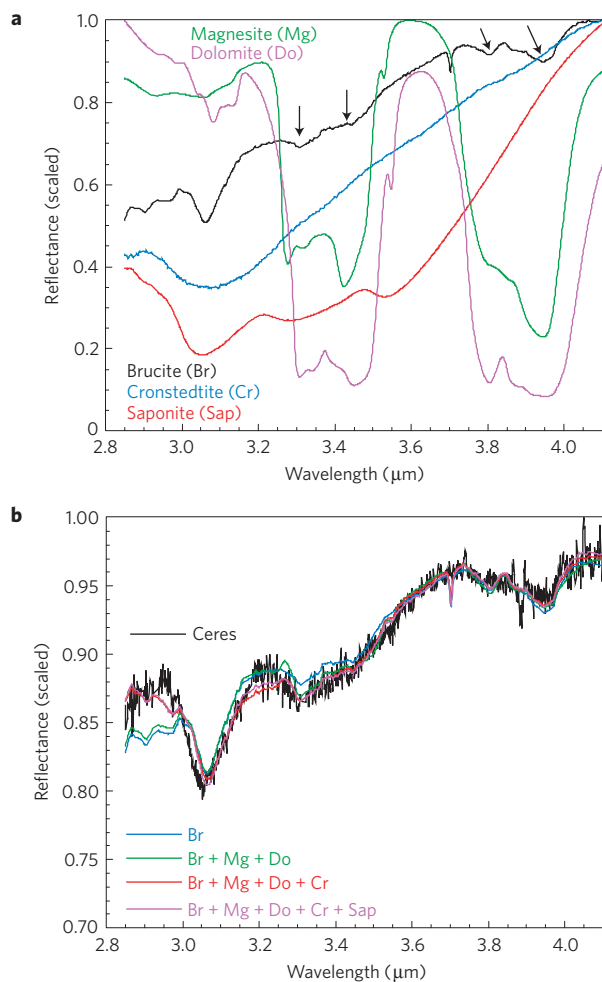
Figure 1 | Linear mixing model results for the near-infrared reflectance spectrum of Ceres. a, Laboratory reflectance spectra of brucite, magnesite, dolomite, cronstedtite and ammoniated saponite were scaled to one at their maximum reflectance point as inputs to the model. The reagent-grade brucite spectrum shows weak spectral features indicative of minor contamination by carbonate (black arrows; Supplementary Information). **b**, Models that used subsets of the endmember spectra produced slightly different results, showing that Ceres' major spectral features can be modelled by the presence of brucite, carbonates and an opaque phase (sloped line). Including cronstedtite in the model improved the fit near 3.4 μm and at wavelengths <3.0 μm, whereas including ammoniated saponite had a negligible effect. See Supplementary Information for sources of spectra.

spectra for brucite, carbonate, magnetite and cronstedtite powders (Fig. 2). Absorptions in the Ceres data can be modelled remarkably well by these components, including features at ~6.4 and ~11 μm that are indicative of carbonates, confirming our results from the near-infrared data. The Ceres spectrum shows a broad absorption feature from ~8–11 μm that is consistent with the presence of brucite and/or cronstedtite. Either phase can model this absorption as long as magnesite and a dark component such as magnetite are also included in the model. Unlike Mg serpentines, cronstedtite shows a strong decrease in reflectance from 7.5–9.5 μm, whereas brucite shows weak features at ~8.3 and ~9.9 μm (ref. 19) that are capable of fitting the observed data when appropriately scaled (Fig. 2). Therefore, Ceres' mid-infrared spectral features can be explained by the presence of carbonate, magnetite and brucite/cronstedtite, whereas spectra of saponite and other smectite clays show trends opposite to those observed for Ceres (Fig. 2).
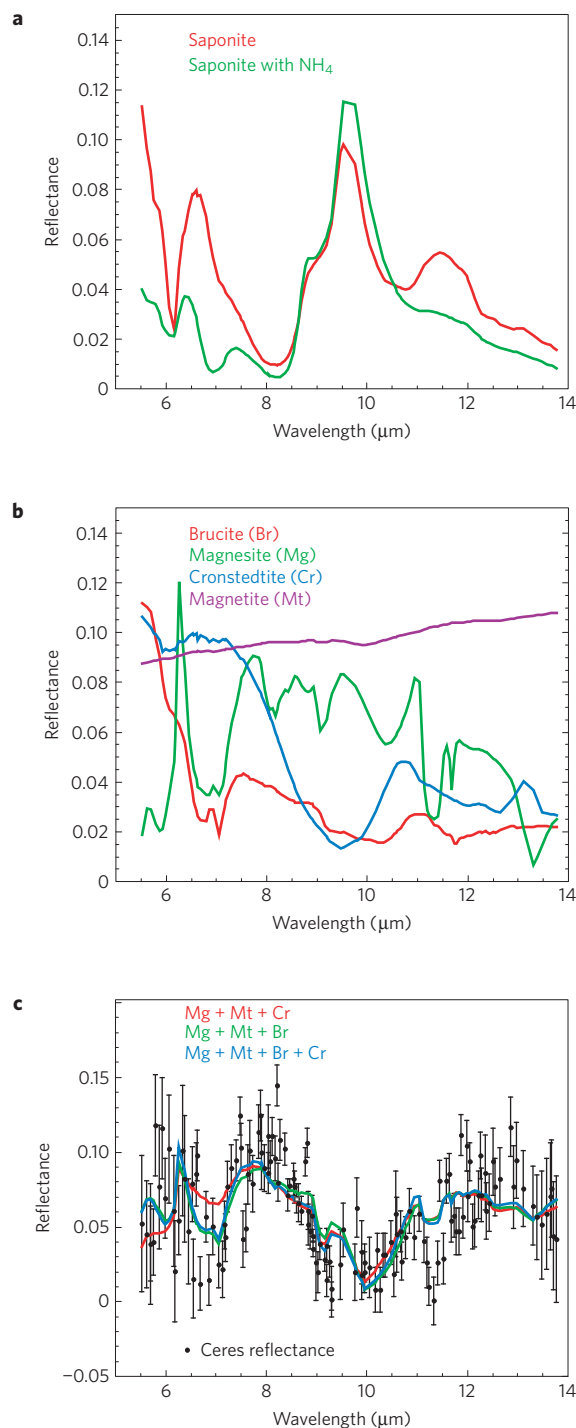

Figure 2 | Linear mixing model results for the mid-infrared reflectance spectrum of Ceres. a–c, Laboratory reflectance spectra of saponite and ammoniated saponite (**a**) are inconsistent with the Ceres data, whereas linear combinations of brucite, magnesite, cronstedtite, and magnetite reflectance spectra (**b**) fit the major features in the Ceres spectrum (**c**). Model results show that the broad absorption centred near ~10 μm can be fitted by either cronstedtite or brucite, but carbonate is required to fit absorptions near ~7 and ~11 μm. Differences in the strength of absorption features between the Ceres and model spectra are probably caused by differences in the particle size ranges and scattering properties between Ceres and the laboratory samples. The mid-infrared Ceres spectrum and associated uncertainties are those published and described in detail in ref. 22.
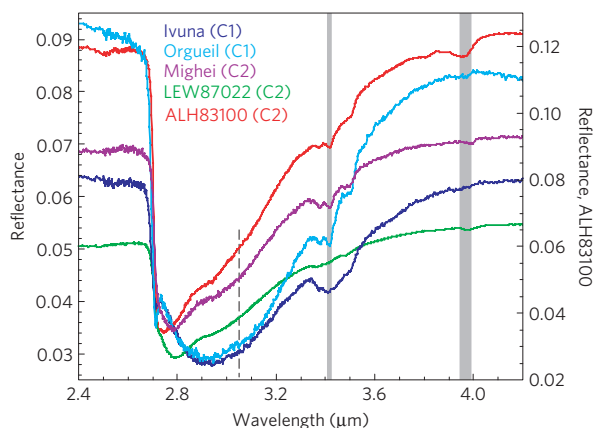
Figure 3 | Reflectance spectra of representative C1 and C2 carbonaceous chondrites. Similar to Ceres, the carbonaceous chondrites are quite dark and show a broad hydration feature in the 3 μm region. In contrast to Ceres, the chondrite spectra lack a feature at 3.06 μm (dashed line), show absorptions due to organic material at ~3.4 μm (narrow grey line) and lack, or show very weak, carbonate features (thick grey line). The carbonate features in chondrite spectra are much weaker than similar features in the spectrum of Ceres relative to other absorptions in this spectral range. This suggests that the optical surface of Ceres contains more carbonate than is found in the C1 or C2 chondrites. See Supplementary Information for sources of spectra.

There is no unambiguous spectral evidence for the presence of organic or inorganic carbon on Ceres, although carbon is an expected component during accretion and aqueous alteration of primitive material. Organics have absorptions near ~3.4 μm and could contribute to this feature in the Ceres spectrum or be masked by the presence of carbonate, but their presence is not required to explain any of the observed spectral features. Although we cannot rule out carbon as an opaque component on the surface, a broad absorption feature centred near ~1.2 μm in the Ceres spectrum is similar to features observed in Fe-bearing phases such as magnetite[9]. The presence of small amounts of opaque phases can have a strong nonlinear effect on suppressing absorption bands at visible–near-infrared wavelengths[23–25]. This effect is evident in laboratory reflectance spectra of C1 and C2 chondrites, which often lack, or show only very weak, carbonate features (Fig. 3). The strength of the carbonate and brucite features in the Ceres spectrum suggests that these phases are major components of the low-albedo surface and that they occur in abundances greater than found in the carbonaceous chondrites. The mixing models also suggest that carbonate is less abundant than brucite, consistent with the relative strengths of their absorption features in Ceres' spectrum (Fig. 1).

A brucite–carbonate alteration assemblage on Ceres is geologically consistent with aqueous alteration of forsteritic olivine and other mafic minerals in a $MgO–SiO_2–CO_2–H_2O$-dominated system. Lesser amounts of cronstedtite and indirect evidence for magnetite as an opaque phase in Ceres' spectrum suggests Fe was also leached from mafic minerals and subsequently oxidized, similar to what is observed in the matrix of carbonaceous chondrites. Brucite and serpentine are expected aqueous alteration products of olivine-rich rocks, such as peridotite[1,26], and the lack of evidence for pure brucite in carbonaceous chondrites and the apparent greater abundance of carbonates on Ceres suggests the alteration pathways and/or parent materials on the dwarf planet were distinct from the meteorites.

Recent studies have shown that Ceres is composed of silicates and a significant fraction of water ice that probably reside in a differentiated interior[1,2]. In these models, a thin silicate and ice crust is underlain by water ice, which in turn is underlain by silicates. Decay of [26]Al provides sufficient heat to melt the water ice,

resulting in differentiation and aqueous alteration of the silicates. Internal temperatures can reach values several hundred degrees above the melting temperature of water ice[1], and hydration of olivine-rich materials at such temperatures would be consistent with the Mg-rich alteration products observed at the surface. It has been suggested that volume expansion due to serpentinization, density contrast between the crust and underlying water mantle, heavy bombardment, cryovulcanism and convection within the ice mantle could all act to destroy the original crust and bring altered materials from depth to the surface[1].

Alternatively, brucite and serpentine may also form on the Earth by interaction of meteoric water with peridotites and other olivine-rich rocks[27]. Therefore, it is possible that the observed phases represent alteration of olivine-rich materials at low temperatures in the crust, similar to the low-temperature aqueous alteration observed in C1 and C2 chondrites. However, models of the thermal evolution of Ceres suggest temperatures in the original crust were never above the melting point of water ice[1], and in this case it is unclear why the alteration assemblage on Ceres would be significantly different from the carbonaceous chondrites. Alteration of olivine-rich material, possibly similar to peridotite, at moderate temperatures beneath the crust or in the deeper interior of Ceres may also explain why brucite is formed on Ceres and not in chondrites, which only have brucite sheets in the form of tochilinite, a phase formed at temperatures <200 °C (ref. 28). The presence of Mg-bearing carbonates on Ceres is consistent with the subsequent interaction of brucite with CO_2-rich fluids, either in the interior or at lower temperatures in the near-surface after excavation from depth. Carbonates in C1 and C2 chondrites, for example, are estimated to form at temperatures as low as 0–25 °C (ref. 29) and the same may be true of carbonates on Ceres.

Differentiation, prolonged interaction between silicates and liquid water at elevated temperatures and the presence of a convective ice mantle may explain why Ceres has apparently experienced more progressive aqueous alteration and is spectrally distinct from chondrites and other smaller, non-differentiated objects in the Solar System. The possibility of altered olivine-rich rocks at Ceres' surface raises questions about the origin of such parent materials and whether it formed by differentiation in the interior or whether Ceres represents accretion of smaller, pre-existing differentiated objects. NASA's Dawn spacecraft will arrive at Ceres in 2015 and carries a suite of instruments capable of testing these hypotheses, including a high-resolution spectrometer that will acquire data over the 0.2–5.0 μm wavelength range[30]. These data will provide further insight into the spatial distribution and diversity of alteration phases on what seems to be a unique and possibly the most aqueously altered primitive body in our Solar System.

Methods

The near-infrared reflectance spectrum of Ceres was modelled using a linear least-squares method. The observed spectrum was modelled as a linear combination of library reflectance spectra of brucite, magnesite, dolomite, cronstedtite and ammoniated saponite (see Supplementary Information for sources of spectra). The linear equation $\mathbf{Ax} = \mathbf{b}$, where $\mathbf{A}$ is the matrix of input library spectra, $\mathbf{x}$ is the vector of coefficients and $\mathbf{b}$ is the observed spectrum of Ceres, was solved inversely for the coefficients in $\mathbf{x}$, which are related to the abundances of each mineral. A line with a positive slope and a line with a negative slope were included in the model in addition to the library reflectance spectra. These lines simulate the presence of opaque phases or other components that affect the spectral continuum slope and the relative strength of absorption features. The laboratory spectrum for magnetite was not used for the near-infrared region because it showed an absorption at 3 μm due to surface-adsorbed H_2O, which would produce erroneous results in this wavelength region. The different sources of the spectra and different particle size ranges of the samples can result in differences in albedo and absorption strengths; thus, the input reflectance spectra were scaled to one at their maximum reflectance point over the modelled wavelength region (2.85–4.1 μm).

The mid-infrared portion of Ceres' spectrum was modelled with the same methods used for the near-infrared data. The absolute emittance data for Ceres[6] were converted to reflectance values using Kirchoff's Law. The spectrum was then modelled using various linear combinations of reflectance spectra for brucite, magnesite, dolomite, magnetite, cronstedtite and ammoniated saponite powders as inputs. Owing to the weaker effects of particle size on overall albedo at these wavelengths, it was not necessary to scale the input spectra before use in the model. Including magnetite in the model acts to adjust the strength of the spectral features, similar to the straight lines used for the near-infrared modelling, thus accounting for most of the variations in absorption strength caused by differences in particle size. The brucite sample was slightly contaminated by carbonate (see Supplementary Information), but it is clear that the major absorptions can be modelled by the presence of carbonate, brucite, cronstedtite and a dark phase such as magnetite.

The unknown composition of Ceres, unknown abundance of opaque phases and complex effects of multiple scattering make it impractical to carry out a full quantitative inverse mixing model. For similar reasons, we did not require that the coefficients sum to unity. Ammoniated saponite can be used to model the $3.06\,\mu m$ feature when it is isolated by continuum removal[10], but this phase provides poor fits compared with brucite when used to model the full 2.85–$4.2\,\mu m$ wavelength range (see Supplementary Fig. S2). In addition, including ammoniated saponite in the model with brucite, carbonate and cronstedtite does not improve the fit to a statistically significant level given the uncertainties in the telescopic data (Fig. 1). We also note that saponite and other smectite clays exhibit spectral features opposite to those observed in the Ceres spectrum over the 6–$13\,\mu m$ wavelength region, further evidence that they are not major components of the surface.

Although the modelled abundances (see Supplementary Table S1) are not directly comparable with true modal abundances, they do indicate that Ceres' spectrum can be modelled as a linear combination of several simple components. The modelled abundances indicate that brucite is a dominant hydrated phase on the surface and is probably at least as abundant as the opaque phase(s) over this wavelength region (see Supplementary Table S1). Carbonates and cronstedtite are present in lesser amounts for the albedo of the opaque component tested here, consistent with their relative absorption strengths in the near-infrared spectrum of Ceres.

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Author contributions

R.E.M. was responsible for writing most of the text and the spectral modelling. A.S.R. contributed to the text, acquired and provided the near-infrared spectrum of Ceres and assisted with interpretation of the results.

Additional information

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