Reports

Evidence for Ammonium-Bearing Minerals on Ceres

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Spectra obtained from recent telescopic observation of 1-Ceres and laboratory measurements and theoretical calculations of three component mixtures of Ceres analog material suggest that an ammoniated phyllosilicate is present on the surface of the asteroid, rather than H_2O frost as had been previously reported. The presence of an ammoniated phyllosilicate, most likely ammoniated saponite, on the surface of Ceres implies that secondary temperatures could not have exceeded 400 kelvin.

The surface mineralogy of the asteroids reflects the initial composition of the parent planetesimal and the effects of endogenic and exogenic processes (*1*). Knowledge of the mineralogy provides information on physical-chemical processes related to asteroid evolution. Ceres is the largest asteroid in the asteroid belt, appears to have suffered aqueous alteration, and may retain its primordial mass (*2*). Samples of Ceres are not represented in the terrestrial meteorite collections, apparently because of the atmospheric entry selection against weak and fast-moving meteoroids (*1*), and therefore it must be studied with remote sensing techniques.

Spectra of 1-Ceres show a broad absorption feature near 3 µm that is characteristic of H_2O. These data suggest that the surface of the asteroid is enriched in phyllosilicates. A narrow absorption feature near 3.07 µm in the Ceres spectrum has been interpreted to imply that there is also a small but significant amount of H_2O frost on the surface (*3*). To evaluate this interpretation and characterize further the mineralogy, we analyzed recent observations of Ceres in the 2.8- to 3.4-µm wavelength region.

Spectra of Ceres were obtained in December 1989 and January 1990 (total of four nights of observations) from the National Aeronautics and Space Administration (NASA) Infrared Telescope Facility at Mauna Kea (*4*). We removed the thermal component from the Ceres spectrum before analysis by determining the overall disk temperature and then by adjusting the wavelength independent emissivity (ϵ) and normalization constant (n) from the standard thermal model to match the geometric albedo of Ceres (*5*). The effective surface temperature for the 2.8- to 4.0-µm wavelength region of the integrated surface area of Ceres is 231.5 K. The thermal component contributed less than 0.3% of the total signal at 3.0 µm and $\sim$24% at 4.0 µm. The reflectance level of the composite Ceres spectrum ranges from 0.04 to 0.05. The thermally corrected spectrum of Ceres was compared to spectra from the U.S. Geological Survey digital spectral library. The 3.07-µm absorption feature cannot be attributed to OH, H_2O, CO_3, SO_4, or other ions containing oxygen in geological materials.

The composite Ceres spectrum was compared to NH_4-bearing mineral species including naturally occurring buddingtonite (NH_4-feldspar) and an NH_4-bearing illite-smectite, as well as laboratory-prepared samples of NH_4-substituted dioctahedral nontronite (Ng-1), a Ca-Na montmorillonite (SWy-1), a ferruginous smectite (SWa-1), and a trioctahedral saponite (SAPCa-1) (*6*). Although all these NH_4-bearing minerals have an absorption feature near 3.07 µm, the feature in the Ceres spectrum is most similar to an NH_4-bearing saponite.

Isolated NH_4^+ belongs to the T_d symmetry group. The triply degenerate ν_3 and ν_4 modes are infrared active. The ν_3 mode produces three absorptions in the wavelength region from 3.0 to 3.6 µm. When it is adsorbed on the surface of the clay minerals, the NH_4^+ ion is distorted because of local surface charge. Thus, there is a shift in the wavelength of the NH_4^+ absorptions in ammonia-bearing minerals relative to the free NH_4^+ ion. The shift is dependent on the crystal structure of the mineral and is thus indicative of the mineralogy.

Saponite is a trioctahedral smectite that commonly forms from hydrothermal alteration or weathering of basic rocks (*7*). Saponite has been reported to be present as an aqueous alteration product in CV and CI carbonaceous chondrites and may be present in CM carbonaceous chondrites (*8*).

Comparison of the ammoniated saponite and saponite show that the strongest NH_4^+ ν_3 fundamental vibration occurs at 3.05 µm in the ammoniated clay and that it is stronger than the fundamental OH absorption,

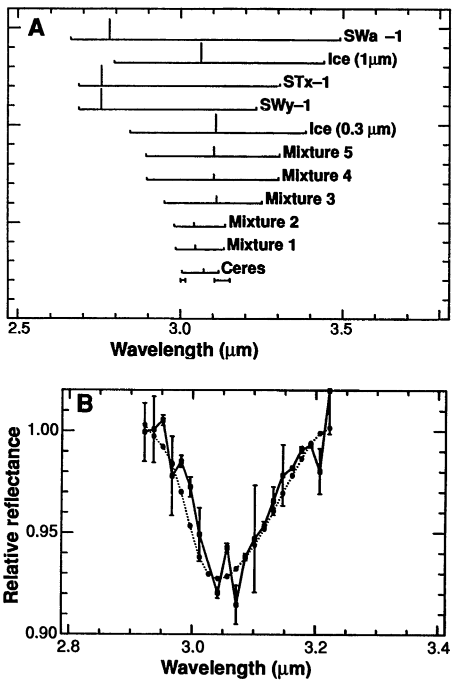

Fig. 1. (**A**) Position of the center, the width, and the asymmetry of absorption features of various materials as well as the 3.07-µm absorption feature on Ceres. The length of the vertical bar (center of absorption feature) for each sample indicates the depth of the absorption feature. Samples included are: SWa-1, a ferrian nontronite; STx-1, a Ca montmorillonite; SWy-1, a Na-Ca montmorillonite (all from the Clay Mineral Repository); and H_2O ice at 1 and 0.3 µm. Computed mixtures are as follows: Mixture 1 is an ammoniated saponite, a black component, and a gray component of 0.07, 0.52, and 0.41% by weight at 2-, 5-, and 10-µm grain size, respectively; Mixture 2 has the same components at 0.05, 0.55, and 0.40% by weight at grain sizes of 3, 5, and 10 µm, respectively. Mixtures 3, 4, and 5 are composed of ice, a black component, and a gray component with the following weight fractions and grain sizes, respectively: Mixture 3 is 0.03, 0.96 and 0.01% at 1, 3, and 30 µm; Mixture 4 is 0.01, 0.98, and 0.01% at 1, 3, and 30 µm; and Mixture 5 is 0.01, 0.98, and 0.01% at 0.3, 3, and 30 µm. Error bars that define the uncertainty of the width of the Ceres absorption are shown below the Ceres plot. The vertical scale is in arbitrary units and is used for illustrative purposes only. (**B**) Results of a least squares fitting (dotted line) of a theoretical mixture (ammoniated saponite (7% by weight), black (52%) and gray (41%) components, at grain sizes of 2, 5, and 10 µm, respectively) to the 3.07-µm absorption on Ceres, which is shown as the solid line with error bars. The fit between the Ceres spectrum and the theoretical mixture is excellent.

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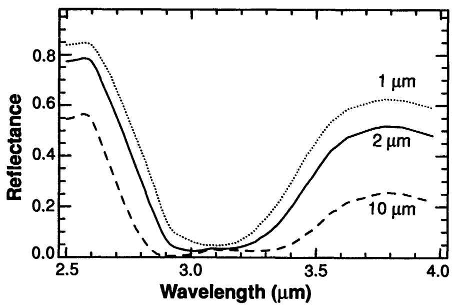

Fig. 2. Calculated spectra of H_2O ice at 1, 2, and 10 µm. The width of the H_2O ice absorption feature and the center of the absorption bands in all three spectra cannot account for the 3.07-µm feature on Ceres (compare with Fig. 1).

which occurs near 2.7 µm. The other two ν_3 absorptions are also seen in the ammoniated saponite, at 3.30 and 3.54 µm, but are weaker than the absorption feature at 3.05 µm and cannot be detected in the spectra of low-albedo objects like Ceres with the current signal-to-noise ratio.

The high-resolution telescopic data indicate that the center of the NH_4^+ absorption on Ceres occurs at 3.07 ± 0.02 µm, compared to 3.05 µm for our laboratory sample. The width of the Ceres absorption is 0.127 ± 0.08 µm, whereas that of the laboratory sample is 0.145 µm. The depth of the 3.07-µm absorption on Ceres is approximately 10% (Fig. 1), and because Ceres is so dark this is indicative of a very strong absorption, stronger than the bound-water absorption features on Ceres.

The 3.07-µm absorption feature on Ceres has been attributed to the presence of H_2O ice (*3, 9*). The H_2O ice grains on the surface of Ceres have been estimated to be approximately 0.01 µm thick if distributed across the entire surface and could not exceed 0.3 µm thick because the absorption feature is not saturated (*3*). However, such a thin layer of ice would not be stable against sublimation for more than a few days (*10*). Two possible explanations for the presence of H_2O frost were given: (i) it is stable in the interlayer position of the phyllosilicate as bound ice or (ii) it is replenished from regolith material by migration of the absorbed H_2O in the phyllosilicates. Analytical models of the H_2O regime of Ceres predict that H_2O ice is not stable anywhere on the optical surface of Ceres (*10*).

Theoretical calculations of H_2O ice spectra at many grain sizes based on radiative transfer reflectance theory (*11, 12*) show that the 3.07-µm absorption on Ceres is much too narrow to be caused by the presence of H_2O ice (Fig. 2). For calculated spectra of H_2O ice at grain diameters of 1, 2, and 10 µm, the width of the 3.1-µm fundamental H_2O ice absorption ranges from 2.8 to 4 times the width of the 3.07-µm absorption in the spectrum of Ceres. In addition, the center of the absorption feature for H_2O ice occurs at longer wavelengths than the 3.07-µm feature in the spectrum of Ceres. Thus, NH_4^+-bearing minerals rather than H_2O ice are most consistent with the 3.07-µm absorption feature.

To understand better the origin of the spectrum of Ceres, we theoretically computed and physically mixed components to mimic the spectrum of Ceres. We computed spectra using the derived optical constants of ammoniated saponite, a black component (low-albedo mixture, 8% reflectance at 2.8 µm for a 1-µm grain size) and a gray component (medium albedo, 28% reflectance at 2.8 µm for a 1-µm grain size). These components were selected to represent assumed albedo levels of surface constituents of Ceres (carbon, organic phases, and mafic silicates). The best spectral agreement was achieved with a mixture of 7% ammoniated saponite by weight (grain size of 2 µm), plus 52% of the black component (grain size of 5 µm), and 41% of the gray component (grain size of 10 µm) (Fig. 1). This computed spectrum produced an absorption feature at 3.07 µm with a depth of 12% versus 10% for Ceres (Fig. 3). The reflectance level of the calculated spectrum is less than 1% lower than the reflectance level of the Ceres spectrum (~0.04 at 3.0 µm). Spectra were also calculated in which H_2O ice at grain sizes of 1 and 0.3 µm was substituted for ammoniated saponite in the three-component mixtures in various proportions. All mixtures with H_2O ice produced spectra with absorption features that were too wide and centered at longer wavelengths than the 3.07-µm Ceres absorption feature (Fig. 1). Increasing or decreasing the grain size of the H_2O ice component did not produce a spectrum similar to that of Ceres (*12*).

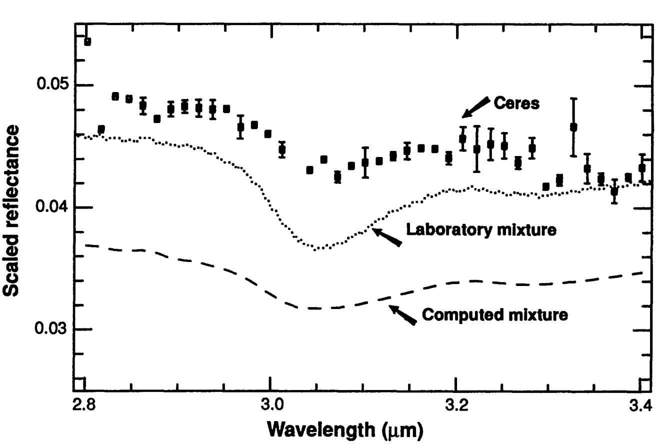

Fig. 3. Spectra of Ceres, a physically mixed laboratory sample, and a theoretically computed three-component mixture. Both mixtures contain ammoniated saponite as one of their components. All three spectra have an absorption feature centered near 3.07 µm and are of comparable strength. The laboratory mixture has been offset in reflectance for comparison.

A physical mixture of ammoniated saponite and carbon black (8% by weight) produced a spectrum that resembles the 2.8- to 3.4-µm wavelength region of Ceres (Fig. 3). However, the reflectance level of the laboratory mixture is too low compared to the Ceres spectrum if the strength of the 3.07-µm feature is correct. This result suggests that the laboratory mixture contains more NH_4 than does Ceres.

Either nonhomogeneous or equilibrium condensation of the solar nebula would provide mechanisms for incorporating NH_4 in Ceres. In nonhomogeneous condensation, ammonium salts and NH_3 ice condense at temperatures below 200 K and form the outermost layer of a planet (*13*). The equilibrium condensation model, however, provides a more appealing method for explaining the origin of ammonia on Ceres. In equilibrium condensation, nebular material with solar elemental composition (*14*) is thought to begin condensing at 1600 K with the formation of refractory oxides and continue until H_2O ices and clathrates formed at temperatures of less than 300 K. Kinetic models (*13, 14*) predict that only limited amounts of NH_3 and CH_4 could be made over the lifetime of the nebula. Thus, there is an enrichment in CO, CO_2, and N_2 greater than the equilibrium amount. At nebula temperatures near 150 K, the temperature at which H_2O ice condenses, ammonium bicarbonate (HN_4HCO_3) and ammonium carmate ($NH_4COOONH_2$) may condense because excess CO, CO_2, and CH_4 are present in the gas phase (*14*).

The formation of phyllosilicates, by hydration of anhydrous materials, would not occur in the nebula at temperatures greater than 300 to 350 K. Recent theoretical work (*15*) suggests that the nebula hydration reaction is kinetically inhibited and that phyllosilicates are secondary alteration products. Thus, fluids to initiate the secondary alteration processes need to be derived internally after condensation and accretion or by impact-generated melting. For small bodies with confining pressures of less than ~1 kbar, heating will produce fluids enriched in

NH_4^+, Na^+, K^+, and Ca^{2+} and salts of CO_3^{2-} and SO_4^{2-} (*13*). This ammoniated water is inferred to react with anhydrous silicates and produce the ammoniated hydrous mineral(s) observed in spectrum of Ceres.

The identification of an ammonium-bearing mineral species, most likely ammoniated saponite, on the surface of Ceres implies that the secondary temperatures cannot have exceeded 400 K. Studies on the stabilities of ammoniated phyllosilicates indicate that the deammoniation of most samples begins at temperatures of ~400 K (*16*). The deammoniation of a phyllosilicate is spectrally detected by decreased intensity and wavelength shifts of the fundamental NH absorptions. The wavelength position of the NH_4^+ absorption on Ceres is similar to that of samples that have not been heated to greater than 400 K. This observation implies that Ceres has experienced minimal thermal reprocessing. Difficulties in obtaining high resolution data with a high signal-to-noise ratio, such as that obtainable with the CGAS spectrometer, for small asteroids with low albedos may be inhibiting identification of additional ammonium-bearing asteroids.

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The Effect of Surface Roughness on Triton's Volatile Distribution

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Calculations of radiative equilibrium temperatures on Triton's rough surface suggest that significant condensation of N_2 may be occurring in the northern equatorial regions, despite their relatively dark appearance. The bright frost is not apparent in the Voyager images because it tends to be concentrated in relatively unilluminated facets of the surface. This patchwork of bright frost-covered regions and darker bare ground may be distributed on scales smaller than that of the Voyager resolution; as a result the northern equatorial regions may appear relatively dark. This hypothesis also accounts for the observed wind direction in the southern hemisphere because it implies that the equatorial regions are warmer than the south polar regions.

TRITON'S SOUTHERN HEMISPHERE IS characterized by normal albedos of 0.8 to 0.9 (*1*) and hemispheric albedos of ~0.8 (*2*). This observation, combined with ground-based measurements of spectral features attributed to N_2 and CH_4 (*3*), strongly suggests that Triton's southern hemisphere is covered with bright N_2 and CH_4 frost. Triton's northern hemisphere is characterized by normal albedos of 0.6 to 0.7 (*1*) and hemispheric bond albedos of 0.5 to 0.6 (*2*). Surface temperatures calculated from regional hemispheric albedos imply that the atmosphere, which is in vapor pressure equilibrium with the surface, should be condensing at most northern latitudes, and thus that the surface should be covered with fresh frost (*3*). Why then is the northern hemisphere darker than the southern hemisphere?

Spencer (*4*), on the basis of an analogy with the Martian southern polar cap (*5*), suggested that frost in the northern hemisphere has been darkened by exposure to sunlight. Moore and Spencer (*6*) suggested that the northern hemisphere appears relatively dark because the N_2 frost has metamorphosized into large transparent ice blocks. This latter view was supported by Eluszkiewicz (*7*) who argued that sintering may create an annealed, transparent nitrogen layer. Both of these hypotheses predict that the south polar and northern equatorial regions of Triton should be buffered to a single temperature by the process of frost sublimation (*8*). However, temperatures inferred from wind directions imply that the equatorial regions are warmer than the south polar regions (*9*). For this to occur some of Triton's northern hemisphere must be devoid of N_2 frost. Thus, it seems likely that the northern hemisphere is warmer and darker than the southern polar cap because of the presence of exposed patches of bare ground, which have a lower albedo than that of fresh frost. Bare ground in this context refers to the underlying surface, which may be composed of water-rich ices that have been darkened by interaction with ultraviolet radiation or energetic particles (*10*).

Here, I adopt as a hypothesis that fresh frost is bright and bare ground relatively dark and explore a mechanism for reconciling the observed albedo pattern and wind directions with the expectation that frost will condense in the cold northern hemisphere. The basic idea is that large-scale albedo patterns can be influenced by small-scale topography. Surface roughness can alter the solar energy deposition over areas smaller than the resolution in Voyager images (roughly 1 km for the highest resolution images) and so affect the distribution of N_2 frost. Areas on the surface that are relatively cold because of their orientation with respect to the sun will also be more difficult to see; thus, bright patches of fresh frost may be hidden. When viewed at low resolution, this type of terrain will have an average albedo that is lower than that of fresh frost and an average temperature larger than the frost temperature. I refer to this effect as small-scale cold trapping.

If frost is bright and bare ground dark, then the southern hemisphere is covered with a large polar cap, whereas in the recent past the northern equatorial region was nearly bare but is now being slowly covered with frost in an inhomogeneous (patchy) manner. Presumably, these are seasonal effects. It was late southern spring on Triton during the Voyager flyby, and the southern polar cap, which was formed in the previous winter, had not had time to evaporate fully. Similarly, all the frost in the northern equatorial regions might have sublimated during the southern winter and spring. The north-

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