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EVIDENCE FOR AMMONIUM-BEARING MINERALS ON CERES; T.V.V. King, R.N. Clark, W.M. Calvin, D.M. Sherman, G.A. Swayze (U.S. Geological Survey, Denver), and R.H. Brown (J.P.L., Pasadena)

Evidence for ammonium-bearing minerals has been found on the surface of the largest asteroid Ceres. This is the first direct evidence for the occurrence of ammoniated-minerals on any planetary body besides the Earth. The presence of ammonium-bearing clays suggests that Ceres has experienced a period of alteration by substantial amounts of an ammonium-bearing fluid. The presence of the ammonium-bearing clays does not preclude Ceres maintaining a volatile inventory in the core or in an volatile-rich zone at some distance below the surface. Recent telescopic observations of Ceres, using the 3.0 meter NASA Infrared telescope facility on Mauna Kea have prompted this reevaluation of its surface mineralogy.

The basis for this study is the use of infrared spectroscopy to make mineralogic identifications on the surface of Ceres using an Earth-based telescope. Spectral reflectance data measures the interaction of light with materials, in this case minerals. Reflectance spectra of minerals have been measured in the laboratory and supplemented with theoretical spectra to provide a library for comparison with telescopic data. Theoretical spectra are derived by applying mathematical formula that incorporate physical constants describing the behavior of various minerals. The interaction of sunlight or "white light" with minerals causes specific wavelengths of the light to be absorbed. The wavelengths absorbed, the intensity of the absorptions and the width of the absorptions are unique from mineral to mineral. The light reflected from each mineral has a characteristic spectrum of wavelengths. The advantage of a theoretical approach is that many more spectra can be derived compared to time-consuming laboratory measurements.

Reflectance data were collected from Ceres, an approximately spherical body with a diameter of 913 kilometers. These spectra were then compared to previously collected laboratory spectra and theoretically-derived spectra in order to identify specific minerals on the surface of Ceres.

Our recent telescopic observations of Ceres indicate an absorption feature at  $3.07 \mu\text{m}$  which we attribute to the presence of ammonium-bearing minerals. This absorption feature was first reported by Lebofsky et al. (1) to occur at  $3.07 \mu\text{m}$  and was believed to be result from the presence of water-ice on the surface of Ceres. However, the wavelength position and the width of the absorption feature on Ceres are very similar to the absorptions resulting from the presence of the ammonium ion in clay minerals.

The spectrum of Ceres was compared to laboratory prepared and naturally occurring clays containing ammonium to determine the best spectral match. Several different structural and chemical types of clays were treated with ammonium chloride. The ammonium-chloride solution interacts with the clay minerals and replaces ions within the clay structure with the ammonium ions. Of the several types of clays tested, the best spectral match for Ceres was an ammonium-bearing saponite. Saponite is a clay mineral which is commonly found on the Earth and commonly forms when basic rocks are altered by hot fluid Weaver and Pollard (2). Saponite is also found as an aqueous alteration product in carbonaceous chondrite meteorites Zolensky and McSween (3); and

references therein).

Comparison of the laboratory spectra and our Ceres data indicate that the ammonium absorption feature on Ceres is centered at  $3.07 \pm 0.02 \mu\text{m}$  vs.  $3.05 \mu\text{m}$  for the ammoniated-saponite. The width of the Ceres absorption feature is  $0.113 \pm 0.08 \mu\text{m}$  vs  $0.145 \mu\text{m}$  for the laboratory sample. The depth of the  $3.07 \mu\text{m}$  feature on Ceres is approximately 8 %.

Previous studies of Ceres have attributed the absorption feature at  $3.1 \mu\text{m}$  to the presence of water-ice. However, theoretical calculations of the water-ice using many different grain sizes are not in accord with this interpretation. For instance, the water-ice at 1 and  $0.3 \mu\text{m}$  grain sizes produces an absorption that is too wide and centered at too long a wavelength to be a good match for the Ceres spectrum.

To help us better understand what materials and how much of each material is necessary to produce Ceres spectrum, we completed two important studies. Firstly, we derived theoretically spectra involving mixtures of three components. Secondly, we measured laboratory spectra of three-component mixtures. We computed a spectrum which had nearly the same brightness and an absorption feature at  $3.07 \mu\text{m}$  which was comparable in strength to that seen in the Ceres spectrum. The mixture simulated the ammonium-bearing clay and included two non-specific minerals to provide dark and medium color. On Ceres we might expect these materials to be a carbon compound and mafic silicates, respectively. We also calculated a spectrum in the same proportions as above, substituting water-ice for the ammonium-bearing clay. The resulting spectra produced an absorption feature which was dominated by a very broad water-ice absorption and does not resemble the spectra of Ceres. Thus, both theoretical and laboratory studies confirm that an ammonium-bearing phase, not water-ice, is an essential component of the Ceres spectra.

Assuming that the asteroid Ceres contains primitive material, then non-equilibrium or equilibrium condensation of the solar nebula could incorporate ammonia into Ceres (Lewis and Prinn (4)). During non-homogeneous accretion, ammonium salts and ammonia-ices condense below  $-70 \text{ C}$  and thus would be incorporated into the outer shell of an accreting object. Equilibrium accretion models assume a solar nebula having solar elemental composition and examine the types of minerals that condense as the nebula cools below  $-1350 \text{ C}$ . As expected, refractory oxides condense first but water ices and hydrates (water ices with various trapped gases) do not condense until the nebula cools below  $30 \text{ C}$ .

In a series of papers, John Lewis and co-workers have demonstrated that only limited amounts of ammonia ( $\text{NH}_3$ ) and methane ( $\text{CH}_4$ ) can be produced during nebula cooling. Importantly, at temperatures near  $-80 \text{ C}$ , when water ice condenses, ammonium bicarbonate and ammonium carmate may also condense. Thus, the potential exists for incorporating ammonium-bearing materials into accreting bodies in the late stage of their growth.

Thus, a body of theoretical evidence predicts that ammonium-bearing phases may be incorporated into the solar system bodies at low temperatures. The question then arises, how does the observation of ammonium-bearing saponite (a clay) fit into this picture? Hydration of anhydrous nebula minerals, to produce clays, within the nebula cannot occur at temperatures above  $30\text{-}80 \text{ C}$

and hydration reactions are very slow. Thus, it seems unlikely that ammoniated-saponite is a primary nebula mineral. A secondary alteration process seems a more likely explanation. Internal heating of Ceres, at temperatures approaching 130 C, may generate fluids enriched in ammonia and other ions, which react with anhydrous silicates to produce secondary clays. The results of such fluid interactions are observed in the carbonaceous chondrites and can be postulated for the Ceres.

(1) Lebofsky, L.A., M.A. Feierberg, A.T. Tokunaga, H.P. Larson, and J.R. Johnson, 1980, *Icarus*, 48, Scientific, 213p. (3) Zolensky, M. and H.Y. McSween, 1988, University of Arizona Press, 114-143. (4) Lewis, J.S. and R.G. Prinn, Academic Press, 470p.

