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Reflectance spectroscopy (0.35–8 μm) of ammonium-bearing minerals and qualitative comparison to Ceres-like asteroids

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ABSTRACT

Ammonium-bearing minerals have been suggested to be present on Mars, Ceres, and various asteroids and comets. We undertook a systematic study of the spectral reflectance properties of ammonium-bearing minerals and compounds that have possible planetary relevance (i.e., ammonium carbonates, chlorides, nitrates, oxalates, phosphates, silicates, and sulfates). Various synthetic and natural NH_4^+-bearing minerals were analyzed using reflectance spectroscopy in the long-wave ultraviolet, visible, near-infrared, and mid-infrared regions (0.35–8 μm) in order to identify spectral features characteristic of the NH_4^+ molecule, and to evaluate if and how these features vary among different species. Mineral phases were confirmed through structural and compositional analyses using X-ray diffraction, X-ray fluorescence, and elemental combustion analysis. Characteristic absorption features associated with NH_4 can be seen in the reflectance spectra at wavelengths as short as ~1 μm. In the near-infrared region, the most prominent absorption bands are located near 1.6, 2.0, and 2.2 μm. Absorption features characteristic of NH_4^+ occurred at slightly longer wavelengths in the mineral-bound NH_4^+ spectra than for free NH_4^+ for most of the samples. Differences in wavelength position are attributable to various factors, including differences in the type and polarizability of the anion(s) attached to the NH_4^+, degree and type of hydrogen bonding, molecule symmetry, and cation substitutions. Multiple absorption features, usually three absorption bands, in the mid-infrared region between ~2.8 and 3.8 μm were seen in all but the most NH_4-poor sample spectra, and are attributed to fundamentals, combinations, and overtones of stretching and bending vibrations of the NH_4^+ molecule. These features appear even in reflectance spectra of water-rich samples which exhibit a strong 3 μm region water absorption feature. While many of the samples examined in this study have NH_4 absorption bands at unique wavelength positions, in order to discriminate between different NH_4^+-bearing phases, absorption features corresponding to molecules other than NH_4^+ should be included in spectral analysis. A qualitative comparison of the laboratory results to telescopic spectra of Asteroids 1 Ceres, 10 Hygiea, and 324 Bamberga for the 3 μm region demonstrates that a number of NH_4-bearing phases are consistent with the observational data in terms of exhibiting an absorption band in the 3.07 μm region.

1. Introduction

Ammonium and ammonium-bearing minerals and compounds are of importance for applications such as understanding the delivery of volatiles to the early Earth, the origins of terrestrial life, the origin and evolution of the Solar System, and astrobiology. For example, the presence of ammonium-rich environments on the early Earth (~2.7 Ga), which may be indicators of early biological processes, is suggested by N isotopic analysis of rocks from the Tumbiana Formation in Western Australia (Stüeken et al., 2015). The presence of ammonium in the solar protoplanetary disk has been suggested on the basis of the presence of subsequently

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formed carlsbergite (CrN) in meteorites (Harries et al., 2015), and ammonium is also expected to form from radiolysis of nitrogen–methane mixtures (Piscitelli et al., 1988). This has implications for delivery of biologically-important compounds to the early Earth. Detection of ammonium in primordial bodies would help to better understand these early Solar System processes and its delivery to the early Earth.

The ability to detect and discriminate between various NH_4^+-bearing minerals also has important astrobiological implications. Ammonium is a potential biomarker since it is often of biological origin, has high thermal stability, and can withstand some level of metamorphism (Boyd, 2001). However, the presence of NH_4^+ is not definitively indicative of biological activity; for example, NH_4^+ could potentially have formed via thermally-processed inorganic amino acids in carbonaceous meteorites (Boyd, 2001). Aqueous activity on asteroidal parent bodies that contain ammonia (and formaldehyde) can lead to the production of prebiotic organic molecules such as amino acids and sugars (Kebukawa et al., 2015).

Ammonium-bearing minerals on Mars has been suggested on the basis of spectroscopic properties of terrains as measured from orbit; this identification is based on the presence of a triplet of absorption bands near 1.07, 1.31, and 1.57 μm (Sefton-Nash et al., 2012). A nitrogen cycle, and possible presence of nitrogen-bearing species on Mars, has been suggested in the past (Manning et al., 2008), although the forms of solid nitrogen-bearing species on Mars are not well constrained (Mancinelli and Banin, 2003). Results to date from the Mars Curiosity rover's Sample Analysis at Mars (SAM) instrument have failed to unambiguously identify the presence of ammonium in surface soils (Wray et al., 2013), although low concentrations of ammonium in soil were reported for the Phoenix landing site (Quinn et al., 2011). Poch et al. (2014) found that various R–NH_2-bearing molecules have half lives on the order of hours or less when exposed to direct Mars-like UV irradiation and surface temperatures and atmospheric pressures (~6 mbar, but under an N_2 rather than a CO_2 atmosphere). Ammonium-bearing oxalate is consistent with the main CO_2 release peaks detected by the SAM results for various targets in Gale crater (Applin et al., 2015). Conversely, analysis of the soluble organic compounds in the martian regolith breccia NWA 7533 failed to detect any N-bearing compounds (Orthous-Daunay et al., 2015). By analogy with the Earth, NH_4-bearing minerals could also form on Mars as fumarolic alteration products (Hausrath and Tschauner, 2013).

The evidence for ammonia on asteroids is more indirect and comes from detection of ammonia in carbonaceous chondrites (Pizarello et al., 2011; Pizzarello and Williams, 2012) and a "high" abundance (395 nmol/g) of methylamine in the Orgueil CI1 carbonaceous chondrite (Aponte et al., 2015). Evidence for the presence of NH_x compounds on comets is more diverse and direct, and includes spectroscopic detection of the dissociation product of ammonia (NH_3) – NH_2 – on four comets (Wyckoff et al., 1991), direct detection of ammonia emission features on comets IRAS-Araki-Alcock (Altenhoff et al., 1983) and Hyakutake (Palmer et al., 1996), and *in situ* measurements of mass peaks near 17 (consistent with NH_3) in the coma of Comet P/Halley by the Giotto spacecraft (Allen et al., 1987). Reconstruction of this observational data suggests ammonia/ammonium abundances up to ~2% (Palmer et al., 1996). Recent spectroscopic measurements of Comet 67P/Churyumov–Gerasimenko (Cappacioni et al., 2015) show little if any contributions from N–H groups in the 3 μm region, where the most intense N–H absorption bands should occur. This finding is not unexpected, as Jupiter Family comets are not predicted to contain appreciable O-free N-rich materials (Dartois et al., 2013). One ultracarbonaceous micrometeorite spectrum presented by Dartois et al. (2013) does exhibit a weak absorption feature near 3.07 μm, consistent with NH_4. Further out in the Solar System, the Cassini spacecraft's Cosmic Dust Analyser detected the probable presence of NH_4^+ molecules in high-velocity dust particles escaping from the saturnian system (Kempf et al., 2005).

Modeling of possible assemblages containing ammonia and ammonium compounds for outer planet icy moons (Enceladus and Titan) suggests that a number of ammoniated compounds would be stable in this region of the Solar System (Marion et al., 2012). Ammonium-bearing phyllosilicates can also readily form via cation exchange (Borden and Giese, 2001). The presence of ammoniated compounds (specifically ammonia ice and ammonia hydrates) is also supported by observational evidence. Ammonia frost has been suggested to be present on satellites in the Saturn system, as evidenced by an absorption band at 2.97 μm (width ~0.612 μm) observed by the Cassini VIMS instrument (Clark et al., 2008, 2012). The presence of this compound combined with the known presence of H_2O ice and CO_2 gives the possibility for the formation of ammonium-bearing minerals, including carbonates and oxalates. Compounds measured by Clark et al. (2012), including some ammonium-bearing minerals, have not yet provided a consistent match to the observational data. Observational data for Miranda (Bauer et al., 2002), Charon (Brown and Calvin, 2000; Cook et al., 2007; DeMeo et al., 2015), Plutino (903482) Orcus (Barucci et al., 2008; Delsanti et al., 2010), and Kuiper belt object (50000) Quaoar (Jewitt and Luu, 2004) suggest the presence of ammonia hydrates and/or ammonia ice, largely on the basis of an absorption feature near 2.21 μm.

Although nitrogen makes up the bulk of Earth's atmosphere, it is present in very low abundance in crustal rocks, and usually occurs as ammonium (NH_4^+) (Busigny et al., 2004). Ammonium-bearing minerals are normally formed by substitution of an alkali cation site within a crystal structure (Krohn et al., 1988; Baugh and Kruse, 1995). Ammonium has an ionic radius (r) of 1.43 Å, and therefore can replace cations having similar ionic radii, such as potassium (K^+) or rubidium (Rb^+), which have $r = 1.33$ Å and 1.47 Å, respectively (Krohn et al., 1988; Marion et al., 2012). Ammonium can also replace Na^+, but to a lesser extent, since the latter has $r = 0.97$ Å (Marion et al., 2012). Among terrestrial minerals, ammonium is commonly found in smectites, micas, illites, alunites, jarosites, and leucites (Felzer, 1990). Mateer et al. (2011) identified lithologies that are most conducive to the incorporation of NH_4^+, including mudstones and siltstones (Williams et al., 1992; Juster et al., 1987), Precambrian metasediments (Boyd and Philippot, 1998; Mingram and Bräuer, 2001), granites (Hall, 1999), and oil shales (Cooper and Evans, 1983).

Terrestrially, ammonium often originates from the decomposition of nitrogenous organic matter, such as proteins and nucleic acids. The decay of organic matter can lead to the release of ammonia or nitrogen, which can eventually be converted to NH_4^+ through biological and thermal processing (Boyd, 2001), and be transported by hydrothermal fluids into a host rock (Hallam and Eugster, 1976; Baugh and Kruse, 1995). However, ammonium can also be formed inorganically as the product of volcanic and intrusive igneous processes (Felzer, 1990; Hausrath and Tschauner, 2013). There are specific hydrothermal alteration processes that enable substitution by NH_4^+, such as sericitic and potassic alteration, which involve minerals with sufficiently high levels of substitutable K^+ (Mateer et al., 2011). Finally, the optical properties of ammonium sulfate are also important for understanding their role in atmospheric radiative forcing (e.g., Li and Min, 2002).

Previous studies of the spectral reflectance properties of NH_4-bearing minerals have been limited to one or a few species (e.g., Krohn and Altaner, 1987; Bishop et al., 2002). Here we expand the range of ammonium-bearing minerals and compounds to include ammonium carbonates, chlorides, nitrate, oxalate, phosphate, silicates, and sulfates. In this study, we analyzed various synthetic and natural NH_4^+-bearing minerals and geologically-relevant