

REMOTE SENSING OF NEAR-EARTH ASTEROIDS
USING NEAR INFRARED (3 μm) SPECTROSCOPY

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ABSTRACT

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Created during the collapse of the solar nebula, asteroids remain as relatively unaltered fragments of the primordial Solar System. The near-Earth asteroid (NEA) population is a relatively easily reachable subset of these widely varying fragments, making them excellent laboratories for testing near-Earth processes that affect airless bodies. Most airless bodies in the inner Solar System are nominally anhydrous as their formation location and lack of an atmosphere generally preclude any form of hydration. The discovery of hydroxide (OH) and/or water (H₂O) on several such bodies raised several questions regarding the ubiquity of water in near-Earth space and its sources. In this dissertation, I investigate the sources of and the various mechanisms by which OH/H₂O is delivered to and/or retained by NEA surfaces to characterize the OH/H₂O budget of near-Earth space to aid in determining the source of Earth's water.

I began by determining the prevalence of OH/H₂O in the NEA population by conducting a 5-year, near-infrared (NIR) spectroscopic survey of these bodies. I used the SpeX NIR spectrometer on NASA's Infrared Telescope Facility (IRTF) to determine asteroid composition and analyze the 2-4- μm spectral region, where absorption features related to O-H bonds are found. Of the 29 NEAs observed, 8 likely contain OH/H₂O on their surfaces, proving OH/H₂O is pervasive in near-Earth space. Three of those 8 NEAs were observed such that I could conduct a detailed analysis of their band depth variations to further understand the OH/H₂O delivery mechanisms. My results indicate that OH/H₂O presence is dependent on asteroid composition and aphelion, as S-complex NEAs that enter the Main Asteroid Belt are more likely to possess a

3- μm feature, and that OH/H₂O appears to be spatially dependent on those asteroids for which the spectral feature of interest was found.

I completed my investigation into OH/H₂O delivery mechanisms by conducting diurnal and annual studies on (101955) Bennu, the target of NASA's OSIRIS-REx mission. I compared spectra collected with the OSIRIS-REx Visible and InfraRed Spectrometer (OVIRS) at different times of day and different points in its orbit to test Bennu's hydration feature for temporal variations I hypothesize would be linked to a secondary source of OH/H₂O. I found clear diurnal and possible annual variations most easily explained by a secondary OH/H₂O delivery mechanism, likely solar wind hydrogen implantation. The combined results across all my investigations strongly suggest that the near-Earth OH/H₂O budget is significantly higher than previously believed and that the mechanisms by which it is delivered are as active now as they would have been in the past.

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I would like to thank my committee members, past and present, for their help both with my research and broadening my scientific perspective. I would especially like to thank my advisor, Josh Emery, who I believe to be the best possible advisor in all of planetary science. His continued guidance and patience have enabled this project to come to fruition and helped me to be a much better scientist than I would have with any other advisor.

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Preface

Chapter 1 entitled “3 μm Spectroscopic Survey of Near-Earth Asteroids” has been written as a paper for The Planetary Science Journal. The work detailed in Chapter 2 is anticipated to be submitted for publication in a peer-reviewed journal. Coauthors will have supported the production of this manuscript and thus this text used “we” to refer to the authors of the upcoming journal article even though data collection, analysis, and writing were all completed by Lauren McGraw. There are some redundancies that come from combining published and soon-to-be published papers in the university format.

1. Introduction

Near-Earth asteroids represent a widely varied population of the most easily accessible relatively unaltered remnants of the primordial Solar System (DeMeo et al. 2015), and as such are excellent laboratories for investigating processes that affect airless body surfaces. One such process, the delivery of volatiles like hydroxide and water (OH/H₂O), was not expected to affect most inner Solar System airless bodies (i.e., those interior to 2.5 au, the 3:1 Jupiter resonance in the Main Asteroid Belt) as they were considered nominally anhydrous. They formed within the frost line, where temperatures and pressures generally would have prevented the formation and condensation of OH/H₂O (e.g., Grossman & Larimer 1974), and lacking an atmosphere causes secondary OH/H₂O to be unstable (e.g., Muralidharan et al. 2008). However, OH/H₂O is required for any habitable world (e.g., Morbidelli et al. 2000) and understanding its prevalence in near-Earth space can aid in determining the source of terrestrial water (e.g., Daly et al. 2021) as well as hazard mitigation and asteroid resource utilization (e.g., Sanchez & McInnes 2012).

1.1 Asteroid Classification

Asteroids are typically characterized by spectral properties in the 0.45- to 2.45- μ m range according to the Bus-DeMeo taxonomic system (Figure 1.1; DeMeo et al. 2009). This system, developed to complement purely visible light taxonomies, divides most asteroids into three complexes that are further subdivided into classes

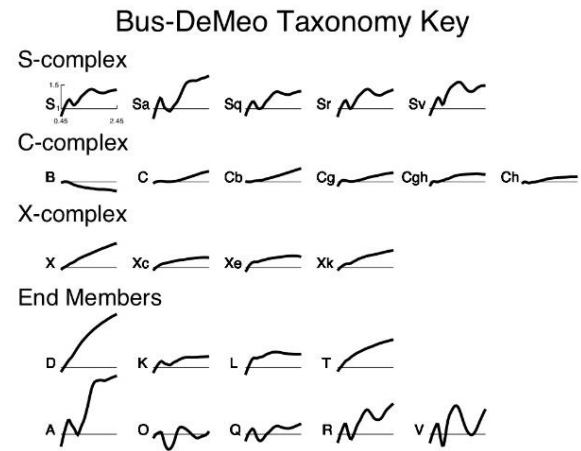


Figure 1.1: Bus-DeMeo asteroid spectral classification (DeMeo et al. 2009).

or types based on spectral differences. S-complex asteroids, so named because they are primarily composed of silicates, exhibit easily identifiable olivine and pyroxene absorption bands at 1 and

2 μm . C-complex asteroids are typically associated with carbonaceous chondrite meteorites and have low surface albedo with nearly to completely featureless, flat spectra. The most common absorption band in the C-complex occurs at 0.7 μm and indicates the presence of phyllosilicates. The X-complex features higher sloped spectra than the C-complex, but still has only subtle to no absorption bands. The X-complex is not compositionally uniform; it includes low-albedo members thought to be carbon-rich, medium-albedo members thought to be metallic, and high-albedo members likely composed of refractory silicates (e.g., enstatite). Finally, several spectral classes do not fit within any of the three defined complexes, such as V-types, which are basaltic and pyroxene-rich. Asteroids described by one of these types are less common than those of the main complexes and typically display more extreme or distinct features (DeMeo et al. 2015).

1.2 Near-Earth Asteroids

Near-Earth Asteroids (NEAs) are defined as having a perihelion of less than 1.3 AU (Binzel et al. 2015). They are typically small inner Main Belt asteroids (MBAs), so are compositionally distributed similarly to the inner Main Belt S-complex asteroids constitute up to 50% of the mass of the inner main belt at sizes smaller than 100 km, with C-complex asteroids increasing in prominence as size decreases (DeMeo et al. 2015). NEA delivery from the Main Belt is a two-step process. All asteroids experience the Yarkovsky effect, which alters the semi-major axis of the asteroid's orbit as the asteroid reemits absorbed solar radiation. This effect is size dependent, and only small objects are perturbed on a geologic timescale. Eventually, the Yarkovsky effect forces an asteroid into resonance with Jupiter or Saturn, which in turn can perturb the asteroid's orbit enough to eject it from the Main Belt into near-Earth space (DeMeo et al. 2015). The semi-major axes at which resonances occur are mostly devoid of solid material and are known as Kirkwood gaps. Most NEAs are expected to have escaped the Main Belt via

the ν_6 secular resonance with Saturn (Froeschlé and Scholl 1986; Binzel et al. 2019).

NEAs are ideal targets for observational studies because at some point in their orbits they approach Earth at significantly smaller distances than MBAs. Though the small size of most NEAs means from the ground they are nominally visible only at their closest Earth approach, they can be brighter than their larger, more distant Main Belt counterparts for a short period of time. Additionally, sending spacecraft to an NEA is significantly cheaper and faster than sending one to an MBA. Studying NEAs is also of high interest to the social and industrial communities because of their potentially dangerous and/or useful natures. Almost 2000 NEAs are currently identified as Potentially Hazardous Asteroids (PHAs) by the International Astronomical Union's Minor Planet Center. PHAs are objects that are capable of approaching Earth to within 0.05 AU and are brighter than 22.0 absolute magnitude (~ 140 m at 14% albedo; NASA's Center for Near Earth Object Studies). Additionally, NEAs' close proximities to Earth make some of them future targets for resource utilization missions. Several private companies have already started their searches for asteroids from which might be produced volatiles for fuel, material for radiation shielding, and substances that are rare on Earth, such as platinum-group metals (Wall 2015). Understanding NEAs can therefore help mitigate the risks associated with a potential impactor, be vitally important to a newly developing industry, and answer many provocative scientific questions.

1.3 OH/H₂O on Asteroid Surfaces

The most efficient method of determining the presence or dearth of OH/H₂O on an asteroid is by conducting near infrared (NIR) reflectance spectroscopy. Water and hydroxide both absorb electromagnetic radiation in the 2-4 μm region due to the stretching of O-H bonds (Gupta 2003). A deep absorption feature is generally indicative of OH/H₂O contained in the

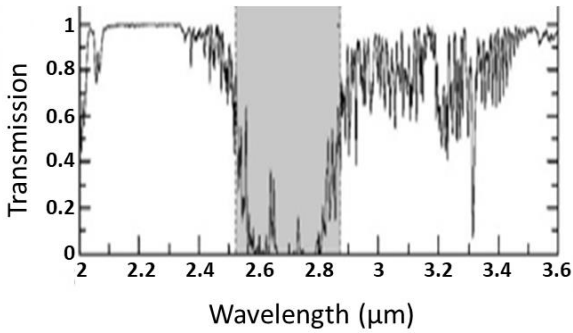


Figure 2.2: Plot of atmospheric radiation transmission versus wavelength showing almost complete absorption between 2.45 μm and 2.85 μm . Modified from Rivkin et al. (2002).

mineral structure, whereas a shallow feature indicates that the molecules are isolated (e.g., Pieters et al. 2009). This wavelength region can be difficult to study using ground-based telescopes, as the band minimum is obscured due to atmospheric water vapor absorbing almost 100% of the radiation between approximately 2.45 μm and 2.85 μm (Figure 1.2). Despite such

difficulties, 3- μm spectroscopy is the best ground-based remote method capable of definitively determining the presence of OH/H₂O.

Recent studies have detected OH/H₂O on nominally anhydrous inner Solar System bodies using NIR spectroscopy. Data from the Deep Impact, Chandrayaan-1, and Cassini missions showed a shallow but clear 3- μm absorption feature on the Moon that was present at all latitudes (Sunshine et al. 2009; Pieters et al. 2009; Clark 2009) and data from the Dawn mission showed that Vesta, one of the largest asteroids in the Main Belt, also exhibits a 3- μm feature and therefore contains water and/or hydroxide on its surface (Prettyman et al. 2012; McCord et al. 2012; Reddy et al. 2012). The NEAs (433) Eros and (1036) Ganymed were also shown to have this spectral feature (Rivkin et al. 2018). These objects are classified as inner Solar System airless bodies, suggesting that this region of space is not as dry as previously thought.

1.4 Delivery Mechanisms

Four potential sources for OH/H₂O on airless bodies have been hypothesized. The first, native phyllosilicates, are only expected on ~5% of NEAs, using estimates from the Main Belt and only on C-complex and M-type (medium-albedo X-complex) asteroids (Rivkin et al. 1995;

Brearley & Jones 1998; Rivkin et al. 2000; DeMeo & Carry 2013; Landsman et al. 2015; Takir et al. 2017) like (101955) Bennu, the B-type NEA that was the target of NASA's OSIRIS-REx mission (e.g., Lauretta et al. 2017; Hamilton et al. 2019). The other three sources of OH/H₂O are exogenous: carbonaceous material, cometary material, and hydrogen implanted via the solar wind. Comets are often thought to have delivered water to several inner Solar System bodies like the Moon and Mercury (e.g., Greenwood et al. 2011; Neumann et al. 2013), and Vesta's 3- μ m features are strongly spatially correlated with low-albedo craters, suggesting hydrated carbonaceous material composed the impactors (McCord et al. 2012; DeSanctis et al. 2012). The final source, solar wind hydrogen implantation, is likely responsible for the global 3- μ m band found on the Moon (Sunshine et al. 2009; Pieters et al. 2009; Clark 2009). Apparent diurnal variations in the band depth correlate with solar orientation (Sunshine et al. 2009; Wöhler et al. 2017; Laferriere et al. 2022), offering a method by which this source of OH/H₂O may be identified. Recent work has also suggested that solar wind implanted hydrogen on asteroid surfaces could have delivered some of Earth's water (Daly et al. 2021).

As solar wind hydrogen implantation should be a continuously active process, the diurnal variations in hydration band depth on the Moon (Sunshine et al. 2009; Wöhler et al. 2017) as well as those detected on some NEAs (Rivkin et al. 2018) indicate active sinks for the created OH/H₂O must be present. Lunar temperatures are sufficient to cause photodesorption of adsorbed hydroxide within 14 hours at the equator (Mitchell et al. 2013); this process should also be active on other inner Solar System bodies. Sputtering can also remove implanted OH/H₂O, though at much slower timescales than for photodesorption (Schaible & Baragiola 2014). Finally, exposure to the vacuum of space can cause rapid evaporation or sublimation of any created OH/H₂O (e.g., Farrell et al. 2017). Exogenous OH/H₂O must therefore be delivered such

that it is resistant to removal and/or in greater quantities than what is easily lost to space. Any object with exogenous OH/H₂O, particularly that delivered by solar wind hydrogen implantation, has reached general equilibrium between addition and removal of OH/H₂O (e.g., Daly et al. 2021).

1.5 Characterizing OH/H₂O on Near-Earth Asteroids

In Chapter 1, I present observations of 29 NEAs and 2 MBAs made using the SpeX near-infrared spectrometer on NASA's Infrared Telescope Facility (IRTF). These observations were made in order to test the hypothesis that OH/H₂O delivery mechanisms active on other objects in near-Earth space should also affect NEAs, thereby producing a 3- μ m feature on these mostly nominally anhydrous bodies. I analyze the shape and depth of the feature to determine the source of any OH/H₂O. I also compare the calculated band depths to various physical and orbital characteristics to ascertain the controls on OH/H₂O delivery and/or retention, in order to create a predictive model of NEAs with OH/H₂O.

In Chapter 2, I present 17 observations of 3 NEAs also made using SpeX on the IRTF to assess 3- μ m band depth variability. As in Chapter 1, I compare the 8 spectra of (433) Eros and 7 spectra of (1036) Ganymed, along with the spectra presented by Rivkin et al. (2018) of these two NEAs, with several physical characteristics and observing and orbital conditions to better understand the cause of the variability. For the third asteroid, (3122) Florence, I use one of the observations to conduct a rotationally resolved study to test for variations in its 3- μ m band. Building on the conclusions from Chapter 1, I aim to predict which OH/H₂O delivery mechanism is active on a body based on observable characteristics from ground-based telescopes.

In Chapter 3, I hypothesize that a component of the deep 2.7- μ m absorption feature on (101955) Bennu is due to solar wind hydrogen implantation. I test this hypothesis by comparing

data taken at different times of day and at different points in Bennu's orbit to assess the band, primarily caused by native phyllosilicates, for any depth or shape variations potentially caused by interactions with the solar wind. I conduct these temporal studies at two sites with different geomorphological characteristics to test for grain size and latitudinal dependencies.

The goal of this dissertation is to characterize OH/H₂O on NEAs by using multiple approaches to better comprehend the OH/H₂O budget of near-Earth space. The work presented here provides the first steps towards predicting OH/H₂O presence and source on nominally anhydrous bodies. This work contributes to the ongoing goal of understanding the source of terrestrial water by studying the current sources of OH/H₂O in near-Earth space and should provide a model by which future asteroid studies and missions interested in OH/H₂O can select targets.

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2. 3 μm Spectroscopic Survey of Near-Earth Asteroids

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Abstract

Near-Earth Asteroids (NEAs) are excellent laboratories for processes that affect airless body surfaces. S-complex (including V-type) NEAs were not expected to contain OH/H₂O on their surfaces because they formed in the anhydrous regions of the Solar System and their surface temperatures are high enough to remove these volatiles. However, a 3- μm feature typically indicative of OH/H₂O was identified on other seemingly dry bodies in the inner Solar System, raising the question of how widespread volatiles may be on NEAs. We observed 29 NEAs using both prism (0.7-2.52 μm) and LXD_short (1.67-4.2 μm) modes on SpeX on NASA's IRTF in order to accurately characterize asteroid spectral type and the 3- μm region. Eight of the observed NEAs have a 3- μm absorption feature at $> 1\sigma$ (3 of which are present to $> 2\sigma$), and they exhibit four identified band shape types. Possible sources for OH/H₂O on these bodies include carbonaceous chondrite impacts and/or interactions with protons implanted by solar wind. Characteristics such as composition and aphelion appear to play an important role in the delivery and/or retention of OH/H₂O, as all eight NEAs with an absorption feature are S-complex asteroids and six enter the Main Asteroid Belt. Additionally, perihelion, size, albedo, and orbital period may play a minor role. Our observations determined that nominally anhydrous, inner Solar System bodies, and therefore near-Earth space in general, contain more OH/H₂O than previously expected. The identified trends should help predict which NEAs that have not yet been observed might contain OH/H₂O on their surfaces.

2.1 Introduction

Volatiles such as hydroxide and water (OH/H₂O) are considered necessary components for

any habitable world (e.g., Morbidelli et al. 2000). Looking for these materials on planetary bodies can aid in assessing their past and future habitability, in addition to determining the OH/H₂O budget of various regions of space. In particular, characterizing OH/H₂O on near-Earth asteroids (NEAs) can aid in explaining how water was delivered to Earth even though it formed within the frost line (Lunine 2006). Most airless bodies that formed (or accreted) in the inner Solar System, that is, interior of the 3:1 Jupiter resonance in the main asteroid belt (2.5 AU), are generally considered to be nominally anhydrous because nebular temperatures and pressures precluded the formation and condensation of volatile-rich materials (e.g., Grossman & Larimer 1974) and the lack of atmospheres preclude the stability of secondary OH/H₂O on their ordinary-chondrite-like surfaces (e.g., Muralidharan et al. 2008). In particular, these bodies formed within the frost line in the Solar System, so water and hydroxide typically could not condense.

Recent studies have detected OH/H₂O on nominally anhydrous, inner Solar System surfaces using 3- μ m spectroscopy, one spectral region in which O-H bonds absorb light. Sunshine et al. (2009), Pieters et al. (2009), and Clark (2009), using data from the Deep Impact, Chandrayaan-1, and Cassini missions, respectively, discovered a shallow but clear 3- μ m absorption feature on the Moon that was present at all latitudes (see Fig. 1C from Sunshine et al. 2009)). More recent work (e.g., Simon et al. 2019; Ruiz et al. 2020; Honniball et al. 2021) has both confirmed and studied the lunar absorption feature in more detail. In 2012, DeSanctis et al. (2012) used data from the Dawn mission to show that Vesta, the largest asteroid in the Main Belt ($a = 2.36$ AU), also exhibits a 3- μ m feature and therefore contains water and/or hydroxide on its surface (see Fig. 2C from DeSanctis et al. 2012). Both Vesta and the Moon are inner Solar System airless bodies, suggesting that bodies in this region of space support surface volatiles, despite their presumably anhydrous formation. Most NEAs formed in roughly the same

environment as Vesta and occupy roughly the same environment as the Moon, so should therefore also contain OH/H₂O on their surfaces. Data from Rivkin et al. (2018) support this hypothesis, with near-infrared (NIR) spectra showing a 3- μ m feature on the two largest NEAs, (1036) Ganymed and (433) Eros, both of which are S-type asteroids and were previously believed to be anhydrous. Identifying the distribution of OH/H₂O within the NEA population will constrain the OH/H₂O budget of the inner Solar System, as well as aid in general compositional understanding of this varied population. Such a study not only aids in understanding Solar System formation, but also hazard mitigation for spacecraft and planetary defense (e.g., Lee 1996, Britt et al. 2002, Opeil et al. 2012, Perna et al. 2013), as well as asteroid resource utilization (e.g., Lewis & Huston 1993, Nichols 1993, Sanchez & McInnes 2012).

2.2 Background

2.2.1 H₂O and OH on asteroid surfaces

Molecular water (H₂O) and/or hydroxide (OH) can be identified on an asteroid by conducting NIR reflectance spectroscopy. Specifically, the bond between an oxygen atom and a hydrogen atom has a fundamental vibrational frequency equivalent to a wavelength between ~2.5 and 3 μ m (e.g., Benedict & Plyler 1951). The band can extend up to ~3.5 μ m, and the exact band center and shape are dependent on the composition and phase of the molecule containing the bonded hydrogen and oxygen (e.g., Rivkin et al. 2002). Band depth is also diagnostic of the nature of the OH/H₂O present, as a deep absorption feature is generally indicative of OH/H₂O contained in the mineral structure, whereas a shallow feature indicates that the molecules are isolated and present in a smaller quantity (e.g., Pieters et al. 2009).

The 2-4 μ m region can be difficult to study using ground-based telescopes, as atmospheric water vapor absorbs almost 100% of the radiation between approximately 2.55 μ m

and 2.85 μm . Despite such difficulties, 3- μm spectroscopy is the best ground-based observing method for remotely determining the presence of OH/H₂O on asteroid surfaces, because the long wavelength edge of the absorption band is still detectable.

2.2.2 Delivery Mechanisms

Four potential sources for OH/H₂O on airless bodies have been previously suggested: native phyllosilicates (e.g., Brearley & Jones 1998), exogeneous carbonaceous material (McCord et al. 2012; DeSanctis et al. 2012), exogeneous/indigenous cometary material (e.g., Greenwood et al. 2011; Neumann et al. 2013; Bottke et al. 2002; DeMeo & Binzel 2008), and solar wind proton implantation (e.g., Zellner et al. 1966; Starukhina 2001; Pieters et al. 2009; Sunshine et al. 2009; Clark 2009). Phyllosilicates compose approximately 21-30% of the Main Belt by mass based on analyses of carbonaceous chondrite meteorites (Brearley & Jones 1998). The Main Belt is ~35-50% C-complex material by mass, though only ~60% of such asteroids contain OH/H₂O (DeMeo & Carry 2013). Other taxonomic classes, primarily M-types, also exhibit a relatively deep ($\geq 10\%$), linearly increasing feature with peak absorption centered around 2.7 μm 3- μm feature that is suggestive of phyllosilicate-bound hydroxide (Rivkin et al. 1995; Rivkin et al. 2000; Landsman et al. 2015; Takir et al. 2017). The mass of phyllosilicates in the NEA population is less constrained due to limited observations in the 2-4 μm region. As NEAs are not uniformly sampled from the Main Belt, they are not a representative population of Main Belt Asteroids (MBAs). Only ~15% are expected to contain phyllosilicates (Binzel et al. 2019), and some NEAs experience high enough temperatures to dehydrate surface phyllosilicates (Marchi et al. 2009), making the actual quantity of phyllosilicates in near-Earth space uncertain. Most NEAs belong to the S-complex (Binzel et al. 2015), which are not expected to contain phyllosilicates.

Carbonaceous and cometary impacts are potential exogenous sources of OH/H₂O on

NEAs. Comets are thought to have delivered water to the Moon and Mercury (e.g., Greenwood et al. 2011; Neumann et al. 2013), so are a potential source on NEAs as well. Additionally, a small percentage (~6-8%) of NEAs are likely of cometary origin (Bottke et al. 2002; DeMeo & Binzel 2008). Absorption features related to comets would be more bowl-like, rather than sharp or linear, due to H₂O being the predominant species over OH (e.g., Rivkin & Emery 2010; Takir & Emery 2012). The Dawn mission revealed numerous impact craters surrounded by low-albedo, hydrated material on the surface of the MBA Vesta (e.g., Prettyman et al. 2012; McCord et al. 2012; Reddy et al. 2012a). Vesta's 3- μ m features are strongly spatially correlated with these dark craters, suggesting hydrated carbonaceous material composed the impactors (McCord et al. 2012; DeSanctis et al. 2012). It is expected that water and/or hydroxide delivered via this mechanism would be correlated with craters on other bodies as well. The features associated with exogenous carbonaceous material vary in shape: one type has an absorption peak at 2.81 μ m and one is very wide with a hard-to-define long-wavelength limit (DeSanctis et al. 2013). Some features appear similar in shape to those of native phyllosilicates, though shallower and with a rounded absorption peak (DeSanctis et al. 2012), while the disk-integrated feature appears as a shallow, zero-sloped feature that steeply increases to the reflected continuum at the long-wavelength end of the band (see Section 2.6.4). Carbonaceous and cometary materials are more common in the outer Main Belt and beyond than in the inner Solar System (e.g., DeMeo & Carry 2013), and carbonaceous/cometary impacts may therefore be expected to be more likely only for NEAs with orbits that take them into the outer Main Belt (i.e., large aphelia).

Solar wind proton implantation offers another method of exogenous OH/H₂O delivery. Features caused by this mechanism most closely resemble that of native phyllosilicates, but much shallower (e.g., Sunshine et al. 2009). The solar wind is primarily composed of hydrogen

ions, and it flows outward from the Sun in all directions at speeds around 400 km/s (Smith 1967). These ions then bombard any surface impacted by the solar wind, which is any surface visible to the Sun that is not protected by a magnetic field or thick atmosphere. OH/H₂O implantation via proton bombardment is a multi-step process. A surface is first mechanically weathered by solar radiation, micrometeorites, or the solar wind, creating crystalline defects and dangling bonds. The vacancies then trap solar wind protons, and if the diffusion time is sufficiently large, the hydrogen ions form bonds with any free oxygen ions to create OH and possibly H₂O that is not necessarily bound to other molecules (Starukhina 2001, 2003, 2006; Farrell et al. 2015, 2017).

Recent laboratory studies, however, suggest that solar wind proton implantation alone is not sufficient to create H₂O, or potentially even OH, without some additional process, such as recombinative desorption or micrometeorite impacts (Burke et al. 2011; Schaible & Baragiola 2014; Orlando et al. 2018; Zhu et al. 2019). Nevertheless, this delivery mechanism is still the most likely responsible for any shallow 3- μ m absorption features on NEAs and is potentially responsible for the 3- μ m signature observed on the Moon, as apparent diurnal variations in the band depth correlate with solar orientation (Sunshine et al. 2009). However, recent work (e.g., Ruiz et al. 2020) suggests the aforementioned diurnal variations are artifacts of inexact thermal tail removal, and properly accounting for various conditions such as surface roughness remove the diurnal variations previously noted. Research into the exact composition, distribution, and delivery of lunar OH/H₂O is ongoing (e.g., Honniball et al. 2021).

Solar wind implanted hydrogen on asteroid regolith might also be a source of terrestrial water. Atom probe tomography studies on a <10- μ m grain of the NEA (25143) Itokawa returned by the Hayabusa mission show that it contains $0.1\text{--}1.6 \pm 0.05$ mol% OH/H₂O and that the depth

of this material within the grain matches those calculated by penetration depth simulations of solar-wind-implanted protons at heliocentric distances experienced by the asteroid. This likely solar-wind-implanted OH/H₂O has a deuterium/hydrogen (D/H) ratio that could help resolve apparent inconsistencies between Earth's oceanic D/H ratio and current hypothesized terrestrial water sources (Daly et al. 2021). Extrapolating that concentration to 100- μ m diameter grains, which is the average diameter for Itokawa regolith (Nakamura et al. 2011; Noguchi et al. 2011, 2014), every cubic meter of Itokawa regolith could contain up to approximately 20 liters of OH/H₂O delivered via solar wind hydrogen implantation (Daly et al. 2021). Though the particle flux of the solar wind was much higher during Solar System formation (Kass & Yung 1995; Ayres 1997) and therefore the rate of OH/H₂O creation was higher, the isotopic profile of the solar wind was the same (Daly et al. 2021), suggesting this mechanism of OH/H₂O delivery could still be impactful to bodies today. Assuming Itokawa is a representative nominally anhydrous S-type asteroid, which is likely the case as analysis of the returned sample confirms the ground- and space-based hypotheses of Itokawa's meteoritical analog (Nakamura et al. 2011), the OH/H₂O quantities suggested by Daly et al. (2021) should be expected on other nominally anhydrous NEAs, making these objects of interest in resource utilization as well as potential sources of terrestrial water. Rough estimates of S-complex asteroid water content suggest that the NEA population of these objects alone could support a crew of 25 for up to 10 years, provided water recycling techniques are used (Sanchez & McInnes 2012). Through the disk-integrated NIR spectroscopic survey of NEAs presented herein, we constrain the variables that control delivery and retention of OH/H₂O to NEA surfaces.

2.3 Methods

2.3.1 Data Acquisition

Spectra were collected using the SpeX instrument on NASA’s Infrared Telescope Facility (IRTF) on Mauna Kea, Hawaii (Rayner et al. 2003). A shallow 3- μm absorption feature, indicative of the presence of O-H bonds, typically has a depth of only a few percent so we targeted a signal-to-noise ratio (S/N) of ~ 50 . The SpeX instrument can achieve the required S/N for asteroids with $V < 14$ mag with two to three hours of integration time. We attempted to observe all NEAs that surpassed this brightness requirement, regardless of spectral type and therefore native composition, since the start of this project in 2016 through 2020, as well as several targets from an earlier preliminary study (Table 2.1), but several objects were not observed due to weather or technical issues. We also observed two Main Belt Asteroids (MBAs) to compare to (1036) Ganymed, one of the NEAs studied. We report here spectra of twenty-nine NEAs and two MBAs.

We used two gratings to fulfill the requirements of this study, both with a $0.8 \times 15''$ slit. The long-wavelength cross-dispersed short mode (LXD_short), which spans 1.67 to 4.2 μm , captures the 3- μm OH/H₂O feature, whereas the prism mode (0.7 to 2.5 μm) enables spectral type and mineralogical determinations. We also used the Guidedog (K-band) and MIT Optical Rapid Imaging System (MORIS; V-band) cameras to track the targets and collect NIR and visible images for future analysis. The observing procedure used requires the telescope to alternate between the NEA and selected local standard star every 10 to 30 minutes to ensure the background noise and absorption features due to telluric water can be adequately removed. The telescope nodded between two positions within the slit when observing both the standard star and target NEA to enable the subtraction of background sky emission.

Table 2.1: Observing parameters & Conditions of NEAs (MBAs at bottom)

Object	Date (UT)	V mag ^a	LXD Mid-time (UT)	LXD Int. Time (s) × Images	Prism Mid-time (UT)	Prism Int. Time (s) × Images	Standard Star	Solar Dist. (au)	Earth Dist. (au)	Phase Angle	Weather ^b (Seeing)
433 Eros	4-Jan-2019	8.3	9:03	30 × 128	6:12	3 × 8	HD 28005	1.153	0.214	34.06	CI (0.5 ^{''})
1036 Ganymed	19-Oct-2011	8.3	10:04	20 × 240	7:50	1 × 16	HD 12846	1.349	0.365	12.82	CI (0.4 ^{''})
1627 Ivar	15-Jun-2018	11.9	9:20	30 × 144	6:39	30 × 16	HD 129290	1.245	0.352	42.99	CI (0.6 ^{''})
1685 Toro	27-Jan-2016	13.1	6:40	20 × 160	8:28	60 × 2	SAO 130276	1.008	0.163	77.15	CI (0.7 ^{''})
1981 Midas	19-Mar-2018	12.4	8:28	30 × 160	5:51	60 × 16	HD 70516	1.042	0.098	59.58	CI (0.5 ^{''})
3122 Florence	4-Sep-2017	9.5	8:58	30 × 116	6:32	8 × 8	HD 197076	1.044	0.052	45.90	CI (0.6 ^{''})
3200 Phaethon	15-Dec-2017	10.4	7:25	30 × 32	...	...	HD 12074	1.038	0.075	42.82	CI, VW (1.8 ^{''})
5143 Heracles	13-Nov-2016	13.3	13:40	30 × 160	10:45	60 × 10	HD 40848	1.177	0.283	43.16	CI (0.8 ^{''})
6063 Jason	7-Jun-2017	14.1	8:05	30 × 80	6:35	120 × 16	HD 135724	1.148	0.183	39.69	PC (0.8 ^{''})
25916 2001 CP44	21-Jun-2018	13.0	10:30	30 × 64	...	...	HD 148729	1.347	0.353	17.60	CI (0.6 ^{''})
54789 2001 MZ7	1-Feb-2010	13.6	12:14	15 × 60	11:02	120 × 8	SAO 97431	1.284	0.305	9.90	CI (0.6 ^{''})
66146 1998 TU3	4-Oct-2017	13.1	14:00	30 × 128	11:18	120 × 4	HD 25710	1.150	0.214	41.46	F (0.6 ^{''})
66391 Moshup	26-May-2019	12.6	...	...	5:36	50 × 8	HD 75023	1.009	0.035	82.88	CI, W (0.7 ^{''})
	29-May-2019	13.0	6:25	30 × 80	...	...	HD 94722	1.024	0.054	76.92	CI, H (1.0 ^{''})
	31-May-2019	13.6	6:15	30 × 86	...	...	HD 101165	1.033	0.074	72.87	CI (0.5 ^{''})
68950 2002 QF15	25-May-2019	14.2	7:22	30 × 154	...	...	HD 96780	1.032	0.101	76.05	CI (0.7 ^{''})
	26-May-2019	14.2	7:43	30 × 126	9:50	60 × 8	HD 98248	1.038	0.107	73.37	CI, W (0.7 ^{''})
85275 1994 LY	7-Aug-2020	14.1	9:42	30 × 128	...	...	HD 163099	1.116	0.158	46.57	F, PaC (0.7 ^{''})
96590 1998 XB	27-Nov-2016	13.4	10:49	30 × 116	8:38	30x2;120x4	HD 23925	1.116	0.144	24.01	PC (0.9 ^{''})
143404 2003 BD44	2-Apr-2017	14.0	8:30	30 × 128	6:17	120 × 4	HD 99252	1.136	0.146	20.11	CI (1.2 ^{''})
144332 2004 DV24	16-Sep-2018	13.1	7:21	30 × 128	9:17	60 × 8	HD 164509	1.013	0.056	80.72	CI (1.1 ^{''})
153201 2000 WO107	2-Dec-2020	13.4	9:41	30 × 192	12:19	70 × 20	HD 283604	1.040	0.054	2.84	W (0.4 ^{''})
159402 1999 AP10	8-Oct-2020	12.6	8:25	30 × 128	10:02	20 × 12	SAO 107923	1.078	0.097	34.39	CI (1.2 ^{''})
	9-Oct-2020	12.6	8:56	30 × 152	...	...	SAO 107932	1.074	0.095	35.96	CI (0.7 ^{''})
163373 2002 PZ39	12-Feb-2020	14.3	8:05	60 × 122	10:31	30 × 8	HD 245025	1.014	0.047	53.70	M CI (-0.7 ^{''})
163696 2003 EB50	24-Nov-2017	13.2	14:07	30 × 116	11:29	120 × 8	HD 268408	1.064	0.101	39.40	CI (0.7 ^{''})
164121 2003 YT1 ^c	30-Oct-2016	15.1	...	...	10:58	10 × 40	HD 36387	1.087	0.210	59.53	MC
194126 2001 SG276	25-Apr-2018	13.0	11:22	30 × 128	8:44	90 × 8	HD 127600	1.091	0.085	3.55	CI (0.7 ^{''})
214088 2004 JN13	30-Nov-2014	13.0	11:11	20 × 280	13:48	60 × 2	HD 34239	1.137	0.174	27.32	CI
285944 2001 RZ11	20-Aug-2014	13.0	10:17	20 × 160	12:21	120 × 4	HD 194764	1.106	0.104	25.12	CI, dry
332446 2008 AF4	10-Jan-2021	14.3	14:10	30 × 198	11:23	70 × 16	HD 101026	1.003	0.034	54.79	CI (1.1 ^{''})
357439 2004 BL86	27-Jan-2015	10.3	12:03	20 × 280	...	...	HD 76332/76765	0.995	0.011	12.67	CI
454177 2013 GJ35	8-Jan-2019	13.8	14:02	30 × 160	16:02	90 × 8	HD 76446	1.176	0.209	21.11	CI (0.6 ^{''})
	14-Jan-2019	13.7	11:26	30 × 176	14:14	90 × 8	HD 71710	1.153	0.193	26.24	CI(0.4 ^{''})
2014 JO25	22-Apr-2017	12.8	8:30	30 × 128	5:43	120 × 4	HD106680	1.056	0.055	23.90	PC (0.8 ^{''})
4 Vesta	2-Apr-2017	7.8	5:42	30 × 8	...	...	HD 60298	2.447	2.071	23.73	CI (1.2 ^{''})
349 Dembowska	10-May-2019	11.3	7:18	30 × 128	9:41	40 × 24	SAO 99090	3.153	2.751	18.08	CI (0.9 ^{''})

Notes.

^a V mag values from JPL Horizons.^b (M)CI—(mostly) clear; CI—cirrus; PC—partly cloudy; MC—mostly cloudy; PaC—patchy clouds; (V)W—(very) windy; F—foggy; H—humid.^c No LXD data for 2003 YT1 owing to poor weather; it is only listed in Tables 1 and 4.

2.3.2 Data Processing

The data were downloaded from the IRTF servers and processed using a variety of IDL-based software tools. The Spextool package (Cushing et al. 2004; Vacca et al. 2003) was used to flat field correct, extract, and wavelength-calibrate spectra from the raw data collected by the telescope. For the LXD spectra, atmospheric absorptions were removed by dividing the extracted NEA frames by the extracted analog star frames observed at similar airmass. A sub-pixel shift was computed and applied before division to assure that the NEA and star frames were properly aligned. For the prism spectra, a grid of ATRAN-derived model atmospheric transmission curves was used to remove the atmospheric absorptions by determining the best-fit transmission model to our data, i.e., varying the water vapor content to match the absorption depth in each NEA and star frame (MacLennan 2019). Sub-pixel shifting and division by the analog star were performed as for the LXD spectra. After division by the star, the spectral frames were combined into a single spectrum. During this step, the individual spectra were scaled to each other before being combined using the standard error robust mean statistical method. Finally, the seven orders of the LXD_short combined spectrum were merged into one continuous spectrum. The Spextool merging code allows the orders to be scaled to each other and lower S/N data at the edges of each order (at wavelengths where contiguous orders overlap) to be trimmed prior to merging (Cushing et al. 2004).

2.3.3 Thermal Tail Removal

The longer-wavelength portion of the LXD spectrum ($\lambda \gtrsim 2.8 \mu\text{m}$, depending on surface temperature) contains a significant thermal component. The thermal tail is removed, after normalization, using a thermal model based on the Near Earth Asteroid Thermal Model (NEATM; Harris 1998). This model, like the Standard Thermal Model (STM), uses the subsolar

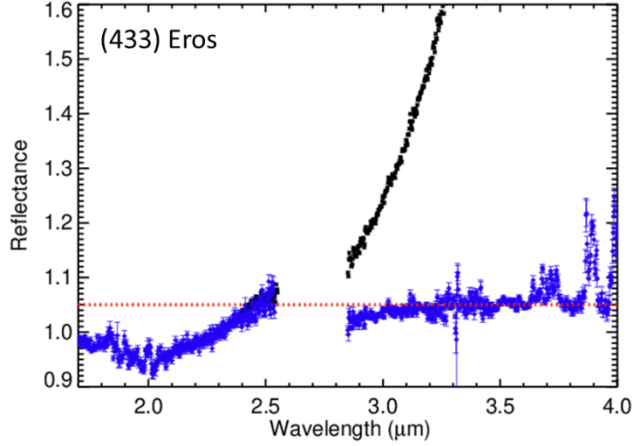


Figure 2.1: Spectrum (normalized reflectance values vs. wavelength in μm) of (433) Eros as observed on 4 Jan 2019. Black data points represent spectrum before thermal tail removal (i.e., reflected and thermal components), blue represents spectrum after thermal tail removal (i.e., only reflected component), and red dashed line represents reflected continuum. Data from 1.7 – 2.55 μm from prism due to noise in LXD data.

temperature ($T_{ss} = \left(\frac{(1-A)*L_0}{4\epsilon\sigma\eta\pi R^2} \right)^{0.25}$) to calculate thermal flux (Lebofsky & Spencer 1989; Harris 1998). The reflected continuum from shorter wavelengths is extrapolated to approximate the linear spectrum at longer wavelengths. The continuum slope and vertical position, along with the beaming parameter in the NEATM, are varied to produce the best-fit continuum, which results in the spectrum at $\lambda > 3.3 \mu\text{m}$ lying along the continuum (Figure 2.1). The band depth,

defined as the difference between the continuum and the reflectance at 2.9 μm , is calculated to determine whether the NEA contains OH/H₂O on its surface. The error in band depth includes propagation of uncertainties from the spectrum and the point-to-point spread in the data.

Additionally, RELAB spectra (1.6 – 4.05 μm) of ordinary chondrite powders were analyzed to verify that continuum slopes selected in this work were reasonable based on meteorite spectra, and to determine an expected standard deviation in continuum slope. While space weathering is expected to increase the spectral slopes of asteroids relative to generally fresh meteorite spectra (e.g., Hapke 2001), the average 2- μm spectral slope of our targets is within 1σ of the average 2- μm spectral slope of the RELAB spectra used in this study. The band depth was recalculated with the $\pm 1\sigma$ continuum for those NEAs with an identified 3- μm feature, and the differences in band depth between the positive and negative 1σ -slopes and the best-fit slope were added in quadrature to the previously calculated uncertainty. For those NEAs without an identifiable 3- μm

feature, the average of this additional uncertainty (0.8%) was added in quadrature to the previously calculated error to account for error in selecting an appropriate continuum.

2.3.4 Band Parameter Analysis

2.3.4.1 Prism Bands

For S-complex and V-type asteroids, the 1- and 2- μm absorption bands in the spectra (BI and BII, respectively) were characterized by the band center wavelengths (BIC and BIIC) and the band-area ratio (BAR). This band parameter analysis was conducted on the prism data using the Band Analysis Routine for Asteroids (BAR-Ast; MacLennan, 2019), an algorithm based on the Spectral Analysis Routine for Asteroids (SARA; Lindsay et al.

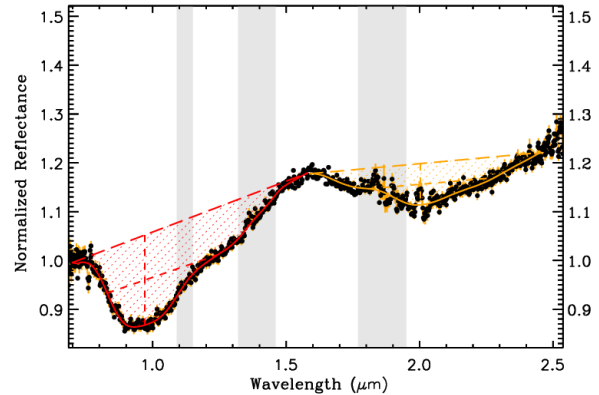


Figure 2.2: Prism spectrum of 433 Eros observed on 04 Jan 2019 showing graphical results of BAR-Ast. The red and yellow shaded regions represent band area. The vertical red and yellow dashed lines mark the band centers, and the slanted red and yellow dashed lines mark the continuum and the FWHM of the bands (MacLennan 2019). The gray shaded bars illustrate spectral regions of telluric water vapor absorptions, which were corrected using ATRAN, as described in section 2.3.2.

2015). SARA uses fifth-order polynomials to define the wavelength minima and maxima of BI and BII, after which it fits third-, fourth-, and fifth-order polynomials to BI and BII to find the band centers and other band parameters. The BAR-Ast algorithm does not assume a polynomial fit to the band, instead using non-parametric smoothing algorithm, producing more accurate results (Figure 2.2; see Fig. 3.4 from MacLennan 2019). The uncertainty of each band parameter is computed using a Monte Carlo simulation, in which reflectance values are randomly sampled from a normal distribution based on the 1σ errors at each wavelength. This study used 10,000 iterations for each NEA to compute the parameters and their 1σ errors.

The relations between band parameters and mineralogy were derived using laboratory

spectra of meteorite samples, so several corrections are required to properly use the equations for asteroid spectra. Temperature is the main factor to address, as the average room temperature on Earth can differ significantly from the temperature of an asteroid's surface. Sanchez et al. (2012) determined that BII is the most susceptible to temperature differences, so both BIIC and the BAR must be corrected. V-type asteroids require two sets of temperature corrections based on composition. Reddy et al. (2012b) found that both BIC and BIIC are affected by temperature differences, but the exact correction depends on whether the asteroid is more similar to a diogenite or a howardite/eucrite. These corrections, as well as the band parameter equations mentioned above, are summarized in Reddy et al. (2015a). The surface temperature of each asteroid is calculated using the globally-averaged equilibrium temperature equation $T_{eq} = \left(\frac{(1-A)*L_0}{16\epsilon\sigma\eta\pi R^2} \right)^{0.25}$, where A is the bond albedo, L_0 is the solar luminosity, ϵ is the emissivity, σ_B is the Stefan-Boltzmann constant, η is the beaming parameter, and R is the heliocentric distance in meters (Burbine et al. 2009). The beaming parameter used in this study was derived from the thermal model described in Section 2.3.3.

Correcting for red edge differences, that is, variations in the maximum wavelength for which reflectance values were collected, is an additional necessary correction between the asteroid and meteorite equations. The BARAst code sets the red edge at 2.45 μm while the red edge of the meteorite spectra used by Dunn et al. (2010) was 2.50 μm . This difference affects the shape of BII and therefore the BAR. Lindsay et al. (2016) determined two new equations for the BAR: one assumes the red edge is 2.45 μm and the other allows for other red edges, though the exact formula depends on which type of ordinary chondrite to which the asteroid is most similar (LL, L, or H). Subsequent work by Sanchez et al. (2020) investigated the dependence of the blue edge (i.e., the short wavelength limit) of BI on BAR and BIC. Additionally, Sanchez et al. (2020)

reduced the S/N of laboratory meteorite spectra to match that of typical asteroid spectra and produced a new set of mineralogical equations taking lower S/N, as well as BI blue edge and BII red edge into account. Differences in band parameters due to phase angle have also been studied, but they do not have a significant impact on mineralogical determinations (Sanchez et al. 2012; Reddy et al. 2012b).

After applying the corrections, the BIC, BIIC, and BAR are then used to make mineralogical interpretations of the silicate asteroids observed (e.g., Gaffey et al. 1993). For ordinary chondrites, the BAR is a proxy for the relative olivine versus pyroxene content (olivine/[olivine + pyroxene]) and BIC is controlled by the fayalite (Fa) and ferrosillite (Fs) content. The BAR does not provide any mineralogical information for V-type asteroids, but both BIC and BIIC can be used to estimate Fs and wollastonite (Wo) content, as well as the magnesium number, which is the ratio of magnesium to the total magnesium and ferrous iron content of a substance. The equations relating band parameters to mineralogy determined for ordinary chondrite meteorites by Sanchez et al. (2020) were used for S-, Sq-, and Q-type asteroids and Burbine et al.'s (2007) equations for HED meteorites were applied to the V-type asteroids.

2.3.4.2 OH/H₂O Band

The depth of the OH/H₂O band is calculated after the thermal tail is removed. The robust mean of the data points surrounding 2.9 μm (2.875 μm – 2.925 μm) is calculated for both the reflected continuum (RC) and the thermally corrected reflectance spectrum (RB). The band depth (BD) at 2.9 μm is calculated by the formula $BD = \frac{RC - RB}{RC} * 100$. Band depth is calculated at 2.9 μm because that value is the closest reliable point in the spectrum to the band center (~2.7 μm) outside of the region with total signal loss due to water vapor in the atmosphere. The error in

the band depth was calculated using standard error propagation techniques, and the error from the choice of continuum is added in quadrature as described in Section 2.3.3. A band is defined as present if the depth is greater than the 2σ error, and a band is defined as potentially present if the depth is greater than the 1σ error. The shape of the 3- μm band, if present, was characterized by plotting band depths, calculated as described above, at 2.95, 3.0, and 3.05 μm along with the band depth at 2.9 μm . Connecting the points created a simplified band shape, which was then used to group NEAs with similar band shapes together.

2.3.5 Statistics

We used the SAS JMP statistics software to conduct statistical analyses in order to search for correlations with band presence and shape type. Specifically, a Student's t-test was used to determine if the mean of the tested continuous variable (ex: diameter, perihelion, etc.) was statistically significantly different between the individual band shape types and between the NEAs with no 3- μm feature. Additionally, the sample used (i.e., all targets, only S-complex, etc.) in the tests was varied to ensure the results were not skewed by S/N or spectral type.

2.4 Results

We made 44 LXD observations of 29 NEAs (Table 2.2; all values except taxonomy from JPL Horizons unless otherwise noted) using the methods described above. We obtained prism spectra for all targets except (4) Vesta, (357439) 2004 BL86, (25916) 2001 CP44, (3200) Phaethon, and (85275) 1994 LY. See Appendix A for spectra of all observed objects. For mineralogical analysis, we used data and/or prism spectra from Frere (2021) for Vesta, Reddy et al. (2015) for 2004 BL86, and the SMASS-MITHNEOS database for 2001 CP44. Mineralogical analysis was not conducted on Phaethon (B-type) and 1994 LY (X-complex). Additionally, we obtained a prism spectrum for (164121) 2003 YT1 but were unable to collect LXD and therefore

3- μm data due to poor weather conditions. The observing and band parameters for 2003 YT1 are listed in Tables 2.1 and 2.3, respectively, but this object is otherwise not discussed in this text. For the NEAs with multiple observations, either only the highest S/N observation is reported herein, or the observations were made in close enough temporal proximity to allow the datasets to be combined, yielding a higher S/N spectrum. In the latter case, all results reported refer to the combined spectrum, though all observations used to create the final spectrum are listed in Table 2.1. Taxonomic classifications were made from the measured prism spectra using the MIT SMASS Bus-DeMeo classification online tool, and we checked and refined our classification using visual comparison to the standard taxonomic types and results from running other available spectra of our targets in the SMASS-MITHNEOS database through the MIT SMASS Bus-DeMeo online tool (DeMeo et al. 2009) to reduce potential inaccuracy in the classification tool caused by noise and/or truncated spectra. The classifications for several NEAs still retain some ambiguity among specific spectral sub-types. Three NEAs exhibit an absorption feature near 3- μm detected at greater than 2σ . Five NEAs exhibit “possible” features for which the detections are between 1 and 2σ . Twenty-one NEAs do not exhibit a detectable 3- μm feature. Ten of these have S/N that is so low that the limit on detection is not terribly meaningful (i.e., 1σ limit on band depth is greater than 5%) (Table 2.3), but 11 spectra have high enough S/N that the non-detections are meaningful in the context of the absence of volatiles from the surfaces.

Table 2.2: NEA and MBA Physical and Orbital Characteristics

	Object	<i>D</i> (km)	Tax.	<i>q</i> (au)	<i>Q</i> (au)	Orb. Per. (yr)	Rot. Per. (hr)	Albedo
433	Eros	16.8	S	1.13	1.78	1.76	5.27	0.25
1036	Ganymed	37.7	S/Sr	1.24	4.09	4.35	10.30	0.24
1627	Ivar	9.1	S/Sq	1.12	2.60	2.54	4.80	0.15
1685	Toro	3.4	Sq	0.77	1.96	1.60	10.20	0.31
1981	Midas	3.4	V	0.62	2.93	2.37	5.22	...
3122	Florence	4.9	Sq	1.02	2.52	2.35	2.36	0.23
3200	Phaethon	6.3	B	0.14	2.40	1.43	3.60	0.11
5143	Heracles	4.8	Q	0.42	3.25	2.48	2.71	0.23
6063	Jason	1.4	Sq	0.52	3.91	3.29	48.6	0.21
25916	2001 CP44	5.7	Sq	1.28	3.84	4.10	4.60	0.18
54789	2001 MZ7	1.6	Xe	1.27	2.29	2.37	37.57	0.86
66146	1998 TU3	2.9	Sq/Q	0.41	1.17	0.70	2.38	0.22
66391	Moshup	1.3	Q	0.20	1.08	0.51	2.76	0.23 ^a
68950	2002 QF15	1.7	Sr	0.69	1.42	1.09	47	0.18
85275	1994 LY	2.5	X	1.05	2.73	2.60	2.70	0.09
96590	1998 XB	0.9	Q	0.59	1.23	0.87	520	0.49
143404	2003 BD44	~1.4 ^b	Sq/Q	0.77	3.16	2.76	78.64	...
144332	2004 DV24	1.2 ^c	Sq	1.01	1.83	1.70	7.99	0.22 ^c
153201	2000 WO107	0.5	X	0.20	1.62	0.87	4.8 ^d	0.13 ^d
159402	1999 AP10	1.0 ^e	Sq	1.01	3.74	3.66	7.91	0.40 ^e
163373	2002 PZ39	0.5 ^c	Q	0.67	2.27	1.78	~149 ^e	0.17 ^c
163696	2003 EB50	1.6 ^c	V	0.76	2.39	1.97	62.4	0.12 ^c
194126	2001 SG276	0.6 ^c	Sq	1.08	1.79	1.71	5.09	0.30 ^c
214088	2004 JN13	2.4	Sq	0.87	4.87	4.87	6.34	0.25
285944	2001 RZ11	1.0	V	1.08	3.30	3.24	2.25	0.41
332446	2008 AF4	0.2 ^c	S/Sr	0.81	1.95	1.63	...	0.40 ^c
357439	2004 BL86	0.3 ^f	V	0.90	2.11	1.84	2.62	0.40 ^f
454177	2013 GJ35	2 ^g	V	1.09	3.19	3.13	...	...
	2014 JO25	~0.8 ^h	Sr	0.24	3.90	2.97	4.53	0.25 ^h
4	Vesta	525.4	V	2.15	2.57	3.63	5.34	0.42
349	Dembowska	139.8	R	2.66	3.19	5.00	4.70	0.38

Notes.

^a Mainzer et al. (2019).^b https://echo.jpl.nasa.gov/asteroids/2014JO25/2014JO25_planning.html^c <http://nearEarthObjects.nau.edu/neosurvey/results.html>^d <https://echo.jpl.nasa.gov/asteroids/1988XB/1988xb.2020.goldstone.planning.html>^e https://echo.jpl.nasa.gov/asteroids/2002PZ39/2002PZ39_planning.html^f Reddy et al. (2015b).^g Warner et al. (2009).^h <https://cneos.jpl.nasa.gov/news/news196.html>

2.4.1 Positive Detections

The three NEAs with a 3- μ m feature are (433) Eros, (1036) Ganymed, and 2014 JO25 (Figure 2.3). Two of the objects have been observed multiple times and by multiple observers in this wavelength range (Ganymed and Eros; Wigton 2015; Rivkin et al. 2018). 2014 JO25 is the smallest of these three NEAs ($d \sim 0.8$ km) and has not been previously studied in this spectral region. It has a band depth of $6.0 \pm 2.9\%$. Eros is the second largest NEA, with a mean diameter of 16.84 ± 0.06 km (Yeomans et al. 2000). It was observed nine times by Rivkin et al. (2018) and seven times in this study; the observation made January 4, 2019, is the only one reported here (a

Table 2.3: NEA and MBA Band Depths and Band Shape Types

Object	3 μm Band?	Band Shape Type	Band Depth (with 1σ Error)
433 Eros	Yes	One	2.5 ± 1.1
1036 Ganymed	Yes	Three	2.7 ± 1.3
1627 Ivar	No	...	1.7 ± 2.3
1685 Toro	No	...	1.8 ± 3.6
1981 Midas	No	...	8.4 ± 9.9
3122 Florence	Maybe	Four	1.9 ± 1.9
3200 Phaethon	No	...	0.5 ± 1.8
5143 Heracles	No	...	1.9 ± 5.6
6063 Jason	No	...	7.0 ± 11.4
25916 2001 CP44	No	...	8.7 ± 14.0
54789 2001 MZ7	No	...	-1.2 ± 6.2
66146 1998 TU3	No	...	-0.9 ± 3.7
66391 Moshup	No	...	0.8 ± 2.4
68950 2002 QF15	No	...	8.1 ± 6.6
85275 1994 LY	No	...	4.8 ± 18.8
96590 1998 XB	Maybe	Four	6.4 ± 4.6
143404 2003 BD44	No	...	8.0 ± 8.9
144332 2004 DV24	No	...	1.6 ± 13.8
153201 2000 WO107	No	...	0.4 ± 1.9
159402 1999 AP10	Maybe	Four	3.5 ± 1.8
163373 2002 PZ39	Maybe	Four	33.8 ± 18.4
163696 2003 EB50	No	...	-2.4 ± 2.4
194126 2001 SG276	No	...	2.2 ± 4.2
214088 2004 JN13	Maybe	Two	3.1 ± 3.1
285944 2001 RZ11	No	...	-0.2 ± 2.1
332446 2008 AF4	No	...	1.8 ± 7.8
357439 2004 BL86	No	...	0.1 ± 1.0
454177 2013 GJ35	No	...	0.1 ± 3.0
2014 JO25	Yes	Four	6.0 ± 2.9
4 Vesta	Yes	Three	2.4 ± 0.9
349 Dembowska	Yes	Three	5.4 ± 2.1

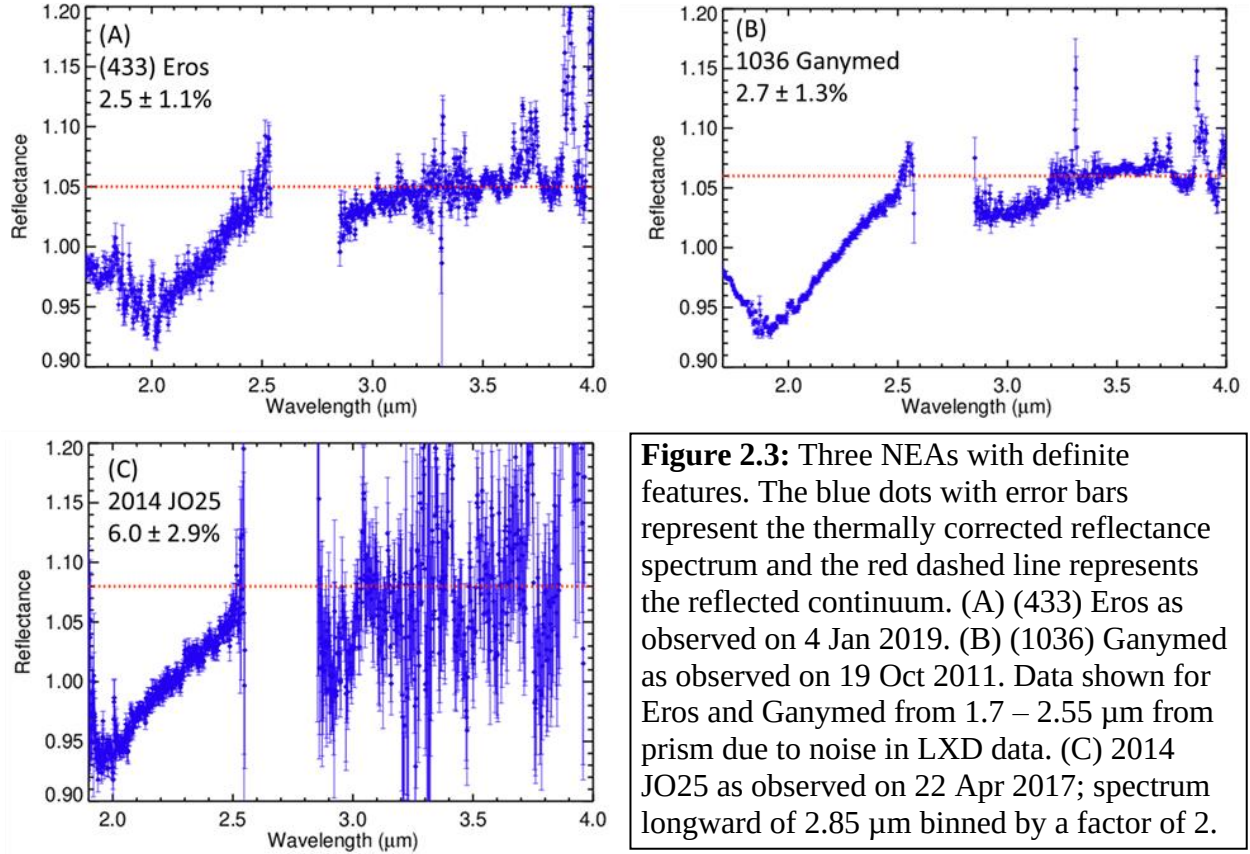
Note. Objects in bold have absorption bands detected at the $\geq 1\sigma$ level and/or a band depth uncertainty of $< 5\%$.

follow-on paper will present the other spectra and analyze variations). Ganymed, the largest NEA ($D = 37.675 \pm 0.399$ km; Mainzer et al. 2016), was observed nine times by Rivkin et al. (2018) and six times in this study; only the observation made October 19, 2011, is reported here (a follow-on paper will present the other spectra and analyze variations). The Eros and Ganymed spectra reported are generally representative of other spectra collected of these two NEAs. Rivkin et al. (2018) found both Eros' and Ganymed's band depth to vary, ranging from $0.0 \pm 2.0\%$ to

$5.0 \pm 2.7\%$ for Eros and $0.0 \pm 1.5\%$ to $6.2 \pm 2.1\%$ for Ganymed. Our band depths for both objects fall within those ranges: Eros' band depth is $2.5 \pm 1.1\%$ and Ganymed's is $2.7 \pm 1.3\%$. The three objects' spectra exhibit three different band shape types, which will be discussed in Section 2.5.1.2.

Both MBAs observed, (4) Vesta and (349) Dembowska, also have a definitive 3- μm feature. Vesta, the archetypal V-type asteroid, has been studied in the 3- μm spectral region by ground- and space-based instruments numerous times (e.g., Hasegawa et al. 2003; Vernazza et al. 2005; DeSanctis et al. 2012; Reddy et al. 2012a). Our observation yielded a band depth of 2.4

$\pm 0.9\%$, which is comparable to the depths seen by Hasegawa et al. (2003) and DeSanctis et al. (2012). Dembowska, a large R-type asteroid, has not been studied in the 2-4- μm spectral region. Our observation yielded a band depth of $5.4 \pm 2.1\%$.



2.4.2 Potential Detections

The five NEAs that potentially have a 3- μm feature are (214088) 2004 JN13, (159402) 1999 AP10, (3122) Florence, (96590) 1998 XB, and (163373) 2002 PZ39 (Figure 2.4). All five have depths that are greater than the 1σ error bars, but less than the 2σ error bars and have spectral shapes that suggest an absorption feature. Nevertheless, given the low S/N of these spectra, we are not completely confident that the features are real. 2004 JN13's band has a different shape from any other target and has a band depth of $3.1 \pm 3.1\%$.

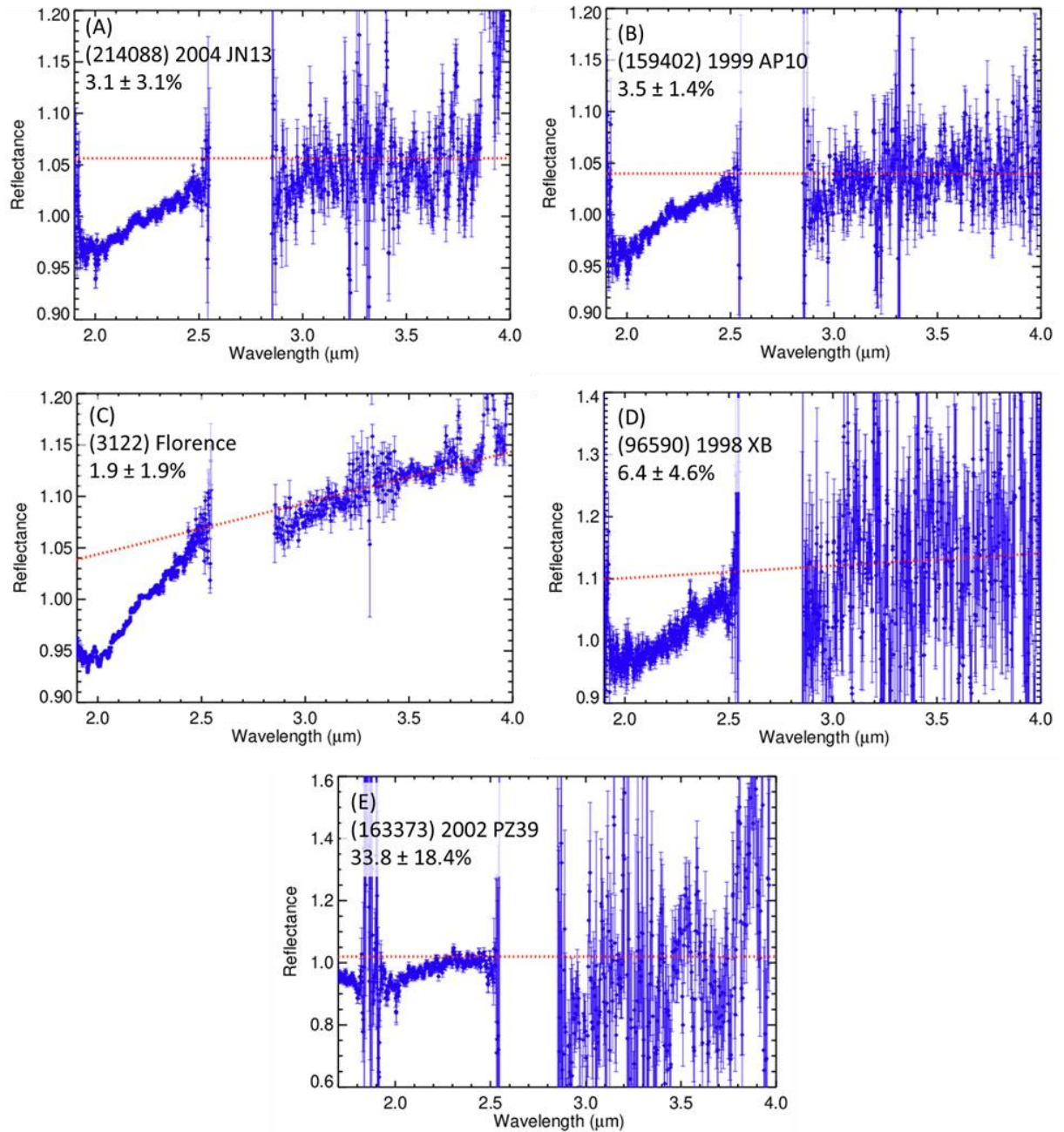


Figure 2.4: Five NEAs with potential features. (A) (214088) 2004 JN13 as observed on 30 Nov 2014; spectrum longward of 2.85 μm binned by a factor of 2. (B) (159402) 1999 AP10 as observed on 8/9 Oct 2020; spectrum longward of 2.85 μm binned by a factor of 2. (C) (3122) Florence as observed on 4 Sep 2017; spectrum longward of 2.85 μm binned by a factor of 3. (D) (96590) 1998 XB as observed on 27 Nov 2016; spectrum longward of 2.85 μm binned by a factor of 2. (E) (163373) 2002 PZ39 as observed on 12 Feb 2020; spectrum binned by a factor of 3.

The other four NEAs with a potential detection exhibit the same band shape type as each other. 1999 AP10 has the strongest band of the four with a band depth of $3.5 \pm 1.8\%$ and is an Sq-type asteroid. Florence is also an Sq-type and has a band depth of 1.9 ± 1.9 . The remaining two NEAs with a potential band are Q-type asteroids: 1998 XB has a band depth of $6.4 \pm 4.6\%$ and 2002 PZ39 has a band depth of $33.8 \pm 18.4\%$. Band shape will be discussed in more detail in Section 2.5.1.2.

2.4.3 Non-Detections

Of the 21 NEAs without a 3- μm feature, 11 of them have spectra with relatively high S/N that rule out bands of depth a few % or greater (Table 2.3; Figure 2.5a). The other ten have spectra that are too noisy to meaningfully confirm the presence or lack of an absorption in the 3- μm region (Table 2.3; Figure 2.5b). A band depth error of approximately 5%, which corresponds to a S/N of 15, was chosen as the cutoff between the two above-mentioned non-detection groups. Detected features generally have a band depth of less than 5% at 2.9 μm , including as seen by Dawn on Vesta (DeSanctis et al. 2012) and on the Moon in some spectra (Clark 2009; Sunshine

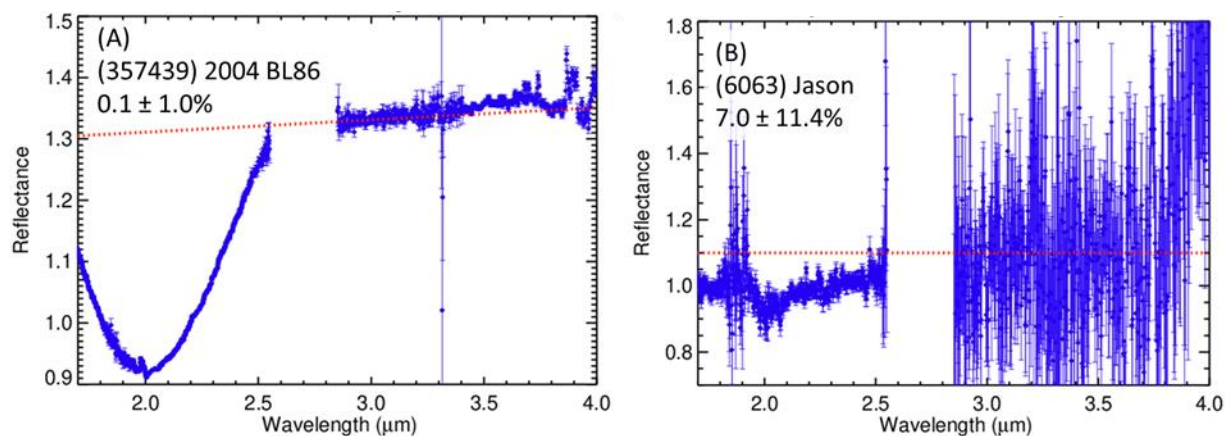


Figure 2.5: (A) (357439) 2004 BL86 as observed on 27 Jan 2015 as an example of a high S/N spectrum showing no detectable absorption feature. (B) (6063) Jason as observed on 7 Jun 2017 as an example of a low S/N spectrum that cannot be used to detect a band with a depth of a few percent typical of OH/H₂O.

et al. (2009) and Pieters et al. (2009) report some deeper features). Additionally, plotting a histogram of S/N averaged over a 0.05- μm wavelength range centered on 2.9 μm showed a gap between spectra with S/N less than 15 and those with higher S/N. The highest S/N spectra of the noisier group of spectra is 12 ((5143) Heracles), with the next highest being 21 ((194126) 2001 SG276). The non-detection NEAs exhibit a wide range of sizes, spectral types, and orbital characteristics though the characteristics sampled were restricted by observational requirements (Figure 2.6).

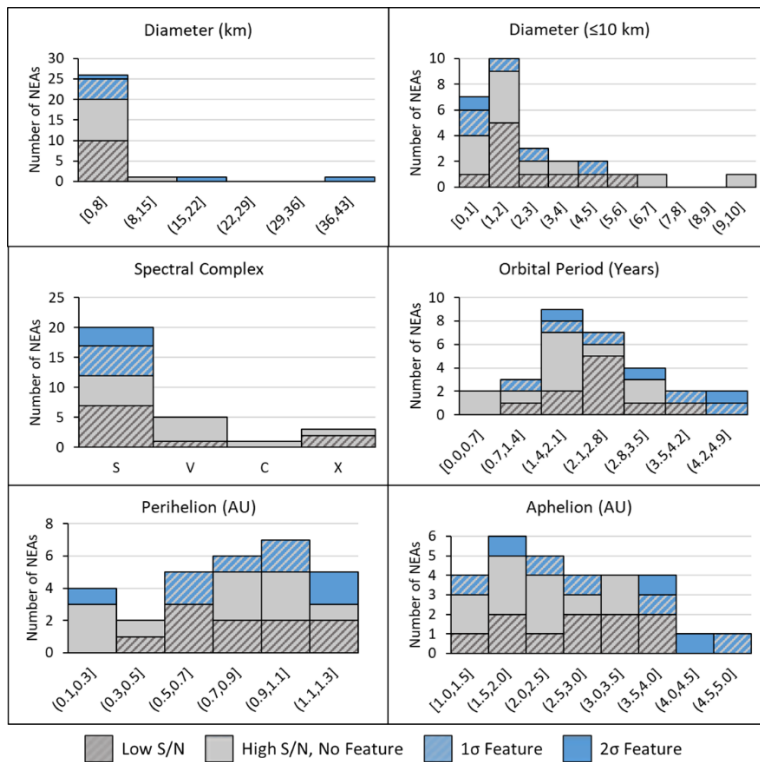


Figure 2.6: Diameter, spectral complex, orbital period, perihelion, and aphelion distributions of surveyed NEAs. Solid blue represents objects with 2.9- μm bands detected to $\geq 2\sigma$ and hashed blue are the objects with 1-2 σ detections. Solid gray represent the NEAs with no detections and upper limits $\leq 5\%$ and hashed gray are the objects with low S/N spectra and no detection.

2.5 Analysis

2.5.1 Band Parameter

Analysis

2.5.1.1 Prism Bands

The temperature-corrected band parameters for all olivine- and/or pyroxene-rich targets (S-complex and V-types) are shown in Table 2.4, as well as red edge- and S/N-corrected mineralogical determinations using the equations presented in Sanchez et

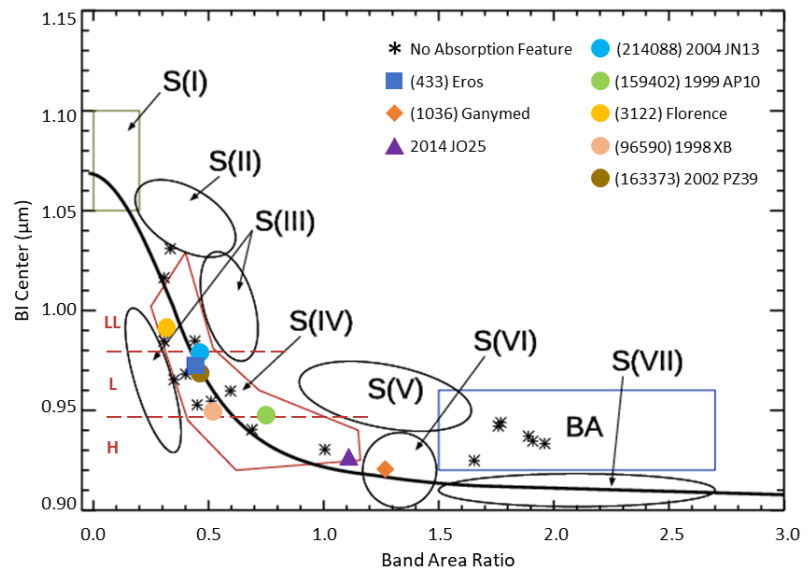


Figure 2.7: Gaffey et al. (1993) S-subtypes plot with ordinary chondrite lines from Dunn et al. (2010). Our objects with definite and possible bands are shown as colored symbols. Our high S/N non-detections are shown as black asterisks. Note that both detections and non-detections occur throughout the ordinary chondrite region (SIV), but the basaltic achondrite (BA) region only contains non-detections.

al. (2020) for S-complex objects and Burbine et al. (2007) for V-types (see Section 2.3.4.1). BIC and BAR are plotted in Figure 2.7 along with different S-complex asteroid sub-types defined by Gaffey et al. (1993). Two S-complex NEAs do not plot in the S(IV) region (Ganymed and 2002 QF15), which is the only region for which the Sanchez et al. (2020) mineralogy equations are intended. Though extrapolating the linear equation for ol/(ol+pyx) should result in greater accuracy for that quantity than extrapolating the parabolic equations for Fa and Fs, using these equations for Ganymed and 2002 QF15 yields Fa and Fs values consistent with H ordinary chondrites (see Figs. 3a & 4a from Dunn et al. (2010) and Fig. 3 from Sanchez et al. (2019)), while the ol/(ol+pyx) results are not (see Fig. 1a from Dunn et al. (2010)). Equations derived specifically for S-complex asteroids that do not plot in the S(IV) region would likely produce

more accurate mineralogical determinations for these two NEA spectra.

Six NEAs plot in the BA (basaltic achondrite) region (V-types; (68950) 2002 QF15 is an Sr-type but also plots in this region), one in the S(VI) region (Sr- and Sv-types), and sixteen in the S(IV) region (pyroxene-poor members of the S-complex). Two of those sixteen NEAs lie along the boundary with the lower S(III) region and one close to the boundary with the S(VI) region. Two plot above the S(IV) region, one of which lies close to the edge of the S(II) region. Seven of the eight NEAs with a detected or potentially detected 3- μ m band plot in the S(IV) region, though 2014 JO25 is the NEA on the border between the S(IV) and S(VI) regions. (1036) Ganymed is the one NEA with a (potential) feature not in the S(IV) region and is instead in the S(VI) region, meaning all eight NEAs with a (potential) feature are S-complex asteroids. Of those in the S(IV) region, three NEAs plot in the LL ordinary chondrite section, ten plot in the L ordinary chondrite section, and three plot in the H ordinary chondrite section, as defined by Dunn et al. (2010).

Our band parameters generally match or are close to previously published results, with some exceptions (Thomas et al. 2014; Dunn et al. 2013; Popescu et al. 2014; Reddy et al. 2022; Aznar et al. 2019; Ieva et al. 2015; Leith et al. 2017). Ganymed's BAR varies in previously published data, causing it to often plot in the S(IV) region, in addition to the S(VI) region (Thomas et al. 2014). Thomas et al. (2014) attributes some of this variation to phase angle, but it is unclear if any of the remaining variation is due to spatial variability. We will investigate potential spatial variability on Ganymed, as well as on Eros and Florence, in an upcoming paper. Our calculated BAR values for Heracles, 2002 QF15, and 2014 JO25 are generally higher than previously published values (e.g., Thomas et al. 2014; Popescu et al. 2014; Dunn et al. 2013; Aznar et al. 2019), significantly so for the latter two objects.

Table 2.4: NEA and MBA Band Parameters

S-Complex Asteroids							
Object		Fa	Fs	ol/ol+pyx	BIC	BIIC	BAR
433	Eros	28.2 ± 2.5	23.7 ± 1.8	0.622 ± 0.040	0.972 ± 0.013	2.012 ± 0.006	0.447 ± 0.009
1036	Ganymed ^a	18.8 ± 2.1	17.2 ± 1.5	0.436 ± 0.041	0.920 ± 0.003	1.960 ± 0.001	1.269 ± 0.030
1627	Ivar	25.4 ± 2.3	21.8 ± 1.6	0.621 ± 0.040	0.953 ± 0.007	1.996 ± 0.002	0.451 ± 0.003
1685	Toro	29.3 ± 2.1	24.6 ± 1.5	0.623 ± 0.040	0.985 ± 0.009	2.063 ± 0.002	0.442 ± 0.002
3122	Florence	29.8 ± 2.0	24.9 ± 1.4	0.652 ± 0.040	0.991 ± 0.004	2.016 ± 0.002	0.317 ± 0.004
5143	Heracles	24.7 ± 2.0	22.0 ± 1.4	0.606 ± 0.040	0.954 ± 0.001	1.945 ± 0.003	0.513 ± 0.004
6063	Jason	26.5 ± 2.0	22.6 ± 1.4	0.583 ± 0.040	0.960 ± 0.002	2.017 ± 0.006	0.610 ± 0.016
25916	2001 CP44 ^b	30.7 ± 2.0	25.5 ± 1.4	0.650 ± 0.043	1.031 ± 0.008	1.961 ± 0.035	0.334 ± 0.150
66146	1998 TU3	27.3 ± 2.0	23.1 ± 1.4	0.644 ± 0.040	0.965 ± 0.002	1.998 ± 0.002	0.351 ± 0.007
66391	Moshup	23.2 ± 2.0	20.3 ± 1.4	0.574 ± 0.040	0.940 ± 0.001	1.977 ± 0.004	0.689 ± 0.009
68950	2002 QF15 ^a	19.8 ± 2.1	17.9 ± 1.4	0.345 ± 0.042	0.925 ± 0.002	1.965 ± 0.007	1.654 ± 0.058
96590	1998 XB	24.9 ± 2.0	21.5 ± 1.4	0.605 ± 0.040	0.950 ± 0.001	2.101 ± 0.001	0.517 ± 0.008
143404	2003 BD44	27.6 ± 2.0	23.4 ± 1.4	0.630 ± 0.040	0.968 ± 0.002	1.981 ± 0.004	0.410 ± 0.012
144332	2004 DV24	29.3 ± 4.3	24.5 ± 3.0	0.655 ± 0.042	0.985 ± 0.036	2.110 ± 0.032	0.307 ± 0.045
159402	1999 AP10	24.6 ± 2.0	21.3 ± 1.4	0.560 ± 0.040	0.948 ± 0.001	1.956 ± 0.014	0.748 ± 0.012
163373	2002 PZ39	27.7 ± 2.0	23.4 ± 1.4	0.617 ± 0.041	0.969 ± 0.003	2.019 ± 0.013	0.467 ± 0.028
194126	2001 SG276	30.7 ± 2.0	25.4 ± 1.4	0.654 ± 0.040	1.016 ± 0.003	2.021 ± 0.002	0.308 ± 0.005
214088	2004 JN13	28.9 ± 2.0	24.2 ± 1.4	0.618 ± 0.040	0.979 ± 0.003	2.024 ± 0.001	0.462 ± 0.008
332446	2008 AF4	21.1 ± 2.0	18.8 ± 1.4	0.499 ± 0.041	0.930 ± 0.002	1.904 ± 0.014	1.006 ± 0.029
	2014 JO25	20.3 ± 2.9	18.2 ± 2.0	0.474 ± 0.040	0.927 ± 0.009	1.964 ± 0.002	1.109 ± 0.014
V- and R-type Asteroids							
Object		Fs	Wo	Mg #	BIC	BIIC	BAR
1981	Midas	50.3 ± 3.2	12.6 ± 1.1	42.4 ± 1.6	0.942 ± 0.001	1.961 ± 0.003	1.759 ± 0.005
163696	2003 EB50	41.4 ± 3.6	9.2 ± 1.3	53.7 ± 2.8	0.933 ± 0.002	1.918 ± 0.001	1.960 ± 0.004
164121	2003 YT1 ^c	43.7 ± 3.2	10.1 ± 1.1	50.8 ± 1.6	0.936 ± 0.001	1.993 ± 0.005	1.889 ± 0.028
285944	2001 RZ11	52.1 ± 3.2	13.3 ± 1.1	40.2 ± 1.6	0.944 ± 0.001	1.975 ± 0.001	1.770 ± 0.002
357439	2004 BL86 ^d	45.2 ± 3.0	10.7 ± 1.0	49.0 ± 6.5	0.937 ± 0.005	1.99 ± 0.01	1.89 ± 0.04
454177	2013 GJ35	42.6 ± 3.2	9.6 ± 1.1	52.2 ± 1.6	0.934 ± 0.001	1.992 ± 0.002	1.908 ± 0.017
4	Vesta ^e	45.1 ± 3.2	10.6 ± 1.1	49.0 ± 1.6	0.937 ± 0.001	1.967 ± 0.002	1.917 ± 0.004
349	Dembowska	53.1 ± 3.2	13.7 ± 1.1	39.0 ± 1.6	0.945 ± 0.001	1.919 ± 0.001	0.961 ± 0.003

Notes.

^a Sr-types that do not plot in the S(IV) region.^b Prism spectrum from SMASS-MITHNEOS public database.^c Only prism data collected.^d Data (except Mg #) from Reddy et al. (2015b).^e BIC, BIIC, and BAR from Frere (2021).

2.5.1.2 OH/H₂O Band

The eight NEAs that have or likely have a 3- μ m absorption feature exhibit four different band shape types (Figure 2.8). Takir & Emery (2012) classified OH/H₂O 3- μ m bands on twenty-eight large, low-albedo (C-complex and P-type) Main Belt Asteroids based on band shape and center (see Figs. 7, 9 – 11 in Takir & Emery (2012)), and their classification also consisted of four groups, though the two sets of groups do not align completely. Eros exhibits a fairly linear feature that sharply increases from $\sim 2.85 \mu\text{m}$ to the reflected continuum around $3.2 \mu\text{m}$. This

band shape type (Figure 2.8a), named here “Type 1,” is nearly identical in shape to Takir & Emery’s (2012) “sharp” group, which composed over 50% of their sample, though their reported feature was typically wider, extending to approximately 3.5 μm , and significantly deeper. This feature is attributed to hydroxide, either in the form of hydrated minerals like phyllosilicates or molecular OH (e.g., Lebofsky 1980). 2004 JN13 also exhibits a feature similar to our Type 1 and Takir & Emery’s (2012) sharp group, though it is much narrower and slightly steeper. This “Type 2” feature is typified by a linear feature that sharply increases from $\sim 2.85 \mu\text{m}$ to the reflected continuum around 3.05 μm (Figure 2.8b).

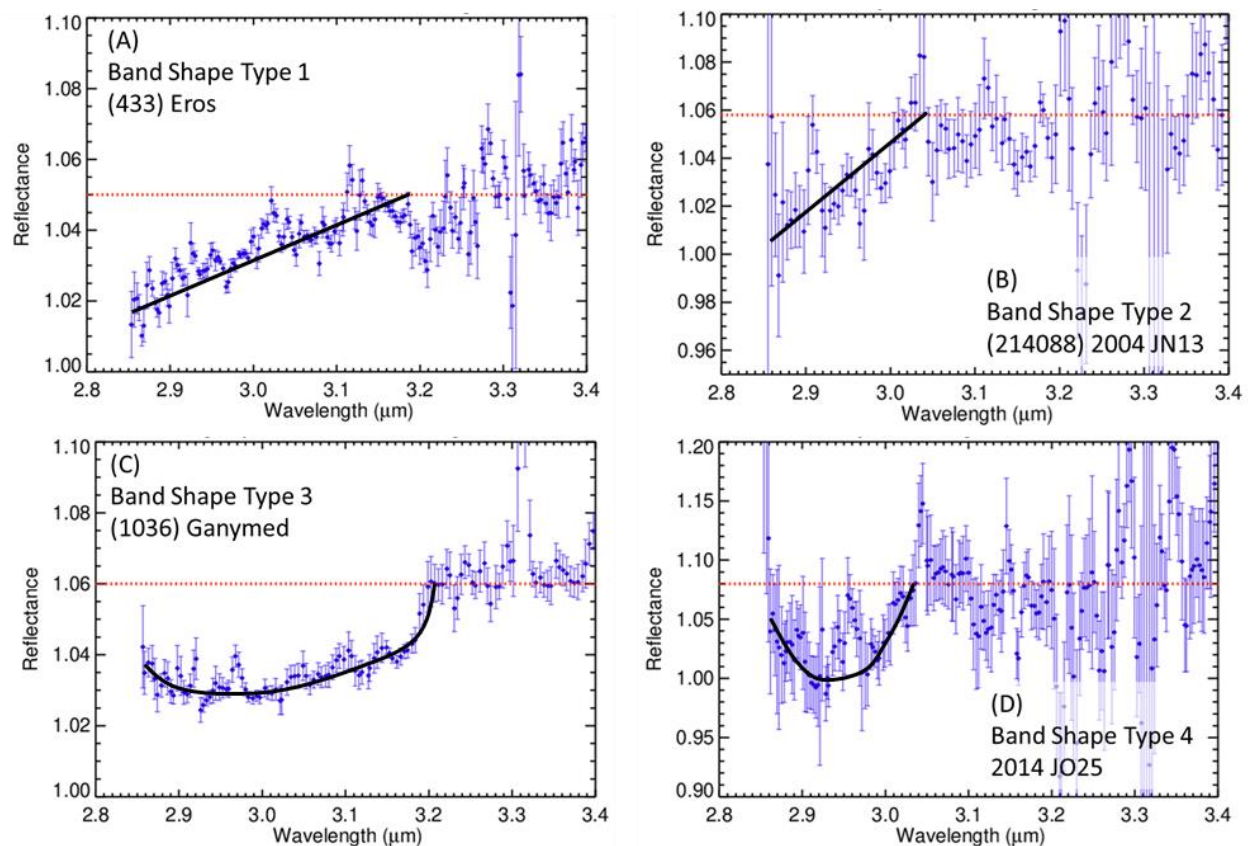


Figure 2.8: Examples of band shape types seen in this survey. Black curves represent model band shape types. (A) Band Shape Type 1; (433) Eros as observed 4 Jan 2019, binned by a factor of 3. (B) Band Shape Type 2; (214088) 2004 JN13 as observed on 30 Nov 2014, binned by a factor of 5. (C) Band Shape Type 3; (1036) Ganymed as observed 19 Oct 2011, binned by a factor of 3. (D) Band Shape Type 4; 2014 JO25 as observed on 22 Apr 2017, binned by a factor of 3.

Ganymed exhibits a rounded, bowl-like feature that is shallow and slightly curved from ~ 2.85 to ~ 3.1 μm before curving more sharply to meet the continuum at ~ 3.2 μm (Figure 2.8c). Labelled as Band Shape Type 3, Ganymed’s feature is most similar to Takir & Emery’s (2012) rounded group, whose feature is attributed to water ice, though our Type 3 does not match Takir & Emery’s classification

Table 2.5: Descriptions of Four Band Shape Types

Band Shape Type	Description	NEAs with Band Shape Type	
1	Wide linear: reflectance linearly increases from 2.8 μm to reflected continuum around 3.2 μm	433	Eros
2	Narrow linear: reflectance linearly increases from 2.85 to 2.95 μm , more shallowly linearly increases to reflected continuum around 3.05 μm	214088	2004 JN13
3	Wide bowl: feature shallow and flat from 2.8 to 3.1 μm , reflectance increases nonlinearly to reflected continuum around 3.2 μm	1036	Ganymed
4	Narrow bowl: feature shallow and flat from 2.8 to 3.0 μm , reflectance increases nonlinearly to reflected continuum around 3.05 μm	3122 96590 159402 163373	Florence 1998 XB 1999 AP10 2002 PZ39 2014 JO25

system as well as our Type 1. Vesta and Dembowska, the two MBAs observed by this study, also exhibit Band Shape Type 3. The other five NEAs – 2014 JO25, 1999 AP10, Florence, 1998 XB, and 2002 PZ39 – exhibit Band Shape Type 4, which is unlike any group described by Takir & Emery (2012), though it, like our Type 3, is most similar to Takir & Emery’s (2012) rounded group. Type 4 is similar to Type 3 but is narrower, with a deeper and more severely curved bowl-shape from ~ 2.85 μm to the reflected continuum at ~ 3.05 μm (Figure 2.8d). Similar to Takir & Emery’s (2012) rounded group, Band Shape Types 3 and 4 increase slightly in reflectance around 2.8 μm , though this pattern is only evident in binned spectra. Takir & Emery’s (2012) Ceres-like feature (broad absorption band from ~ 2.8 to 3.7 μm with a superimposed band at 3.05 μm) and Europa-like feature (similar to Ceres-like but with a superimposed band centered at 3.15 μm) are not represented in our sample of NEAs. The four band shape types are summarized in Table 2.5.

2.5.2 Target Comparisons

We searched for trends between the presence of a 3- μm band and several physical and

orbital characteristics in order to identify any differences between the population of NEAs that have and do not have a 3- μm feature. Quantities such as perihelion, composition (including spectral type, band slopes, and mineralogy from band parameters), diameter, aphelion, rotation rate, heliocentric distance, Earth and Jupiter MOID, Main Belt source regions, orbital eccentricity, orbital inclination, orbital period, and time since perihelion passage were compared against the band depth at 2.9 μm . Of those, only aphelion (Figure 2.12) and composition show strong trends. Diameter (Figure 2.9), perihelion, orbital period, and albedo appear to be weakly correlated with the presence of a 3- μm band.

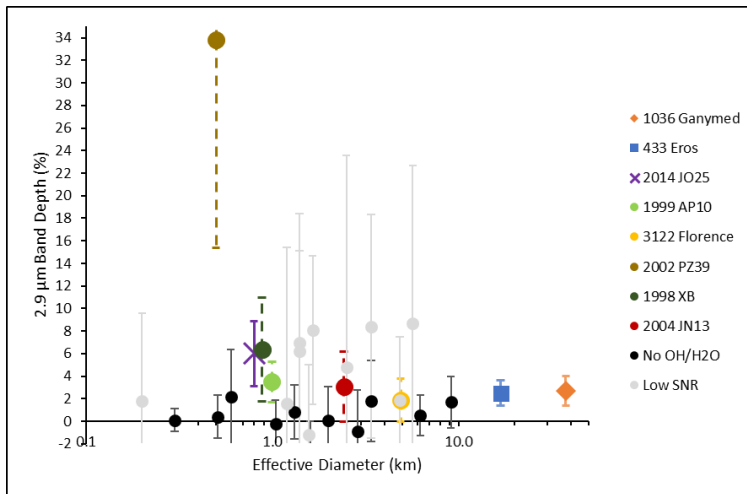


Figure 2.9: Band depth plotted against effective diameter. Larger NEAs tend to have a 3- μm feature, though the trend is non-unique.

The two largest NEAs (Eros and Ganymed, mean diameters of ~ 17 and ~ 38 km), both in our sample and in the entire population of NEAs, exhibit a 3- μm feature, while most of the other NEAs in our sample with no feature are smaller than 5 km. However, the other six NEAs with (potential) features are

also smaller than 5 km. The possible trend with diameter is therefore non-unique, even though the diameters of Eros and Ganymed are large enough to statistically differentiate them from the mean diameters of the other NEAs. With respect to perihelion distance, most of the NEAs with no 3- μm feature have $q \lesssim 1$ AU, while both Eros' and Ganymed's perihelia are greater than 1.1 AU. This apparent trend, like with diameter, is also non-unique, as the other six NEAs with a (potential) feature also have $q \lesssim 1$ AU. Likewise, the objects with the largest orbital periods

(~4.6 years), 2004 JN13 and Ganymed, both exhibit a (potential) feature, while the rest of the NEAs in our sample have orbital periods statistically significantly shorter, regardless of the presence of a band. No other trends discussed in this section were statistically significant.

The non-unique trends in diameter (Figure 2.9), perihelion, and orbital period discussed above, as well as in albedo, are slightly

strengthened when considering only the NEAs exhibiting Band Shape Type 4 and those with no band, particularly when the population of NEAs with no band is limited to certain subsets (Figure 2.10). These trends are strongest when comparing the Band Shape Type 4 NEAs to the S-complex NEAs with higher S/N spectra.

Higher S/N NEAs with no band tend to be larger than the Type 4 NEAs, over two times larger in the case of higher S/N S-complex NEAs with no band, but the 1σ error bars on these means suggests diameter is only weakly correlated with

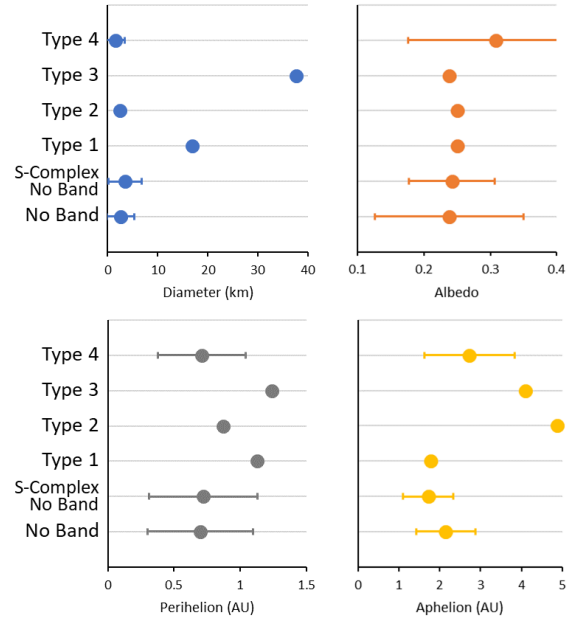


Figure 2.10: Only higher S/N NEAs are included in the data points for NEAs with no band. Error bars are standard deviations of the objects of that type. Points with no error bars have only a single object of that type.

the presence of a band. More observations are required to determine if this diameter trend is real or a result of larger objects being brighter, resulting in higher S/N spectra. Similarly, the Type 4 NEAs tend to have slightly larger perihelia, but the substantial overlap in values between the Type 4 NEAs and those higher S/N NEAs with no band weakens the significance of perihelion. Type 4 NEAs also tend to have larger orbital periods and albedos than higher S/N S-complex NEAs with no band, as the means are 74% and 35% larger, respectively.

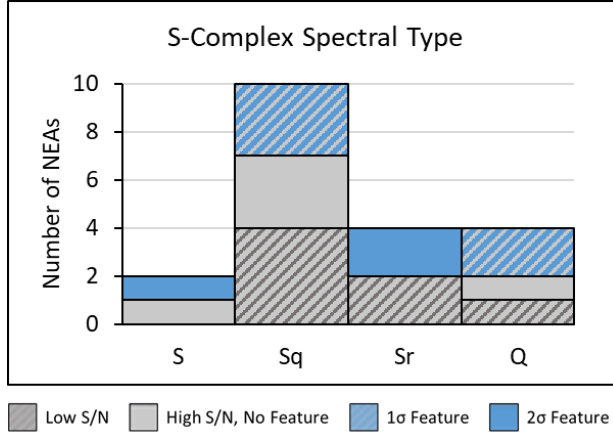


Figure 2.11: Histogram of S-complex spectral types observed in this study. Solid blue represents objects with 2.9- μm bands detected to $\geq 2\sigma$ and hashed blue are the objects with 1- 2σ detections. Solid gray represent the NEAs with no detections and upper limits $\leq 5\%$ and hashed gray are the objects with low S/N spectra and no detection.

Trends in band presence with composition and aphelia are much more robust. As described in Section 2.5.1.1, all eight NEAs with a (potential) feature are in the S-complex (Figure 2.11): one is an S-type, three are Sq-types, two are Sr-types, and two are Q-types. We observed one C-complex NEA, three X-complex NEAs, and five V-type NEAs, none of which exhibit a feature in the 3- μm region, though one of the V-types and two of the X-complex NEAs have band depth

uncertainties larger than the cutoff described in Section 2.4.3. When restricting the sample set to only those NEAs in the S-complex with higher S/N spectra, only four of the twelve NEAs show no indication of a 3- μm band. No trend in Fa, Fs, or olivine ratio with band presence or shape is detected.

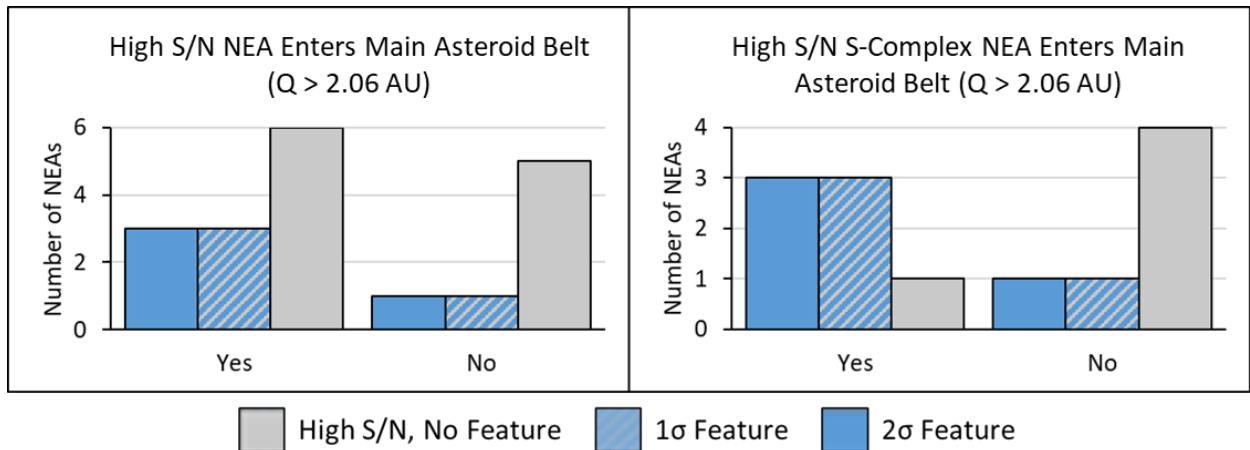


Figure 2.12: (Left) Histogram of all higher S/N NEAs binned by whether they enter the Main Belt. (Right) Histogram of higher S/N S-complex NEAs. Solid blue represents objects with 2.9- μm bands detected to $\geq 2\sigma$ and hashed blue are the objects with 1- 2σ detections. Solid gray represent the NEAs with no detections and upper limits $\leq 5\%$.

The trend with aphelia is slightly more complicated, but still evident when looking only at higher S/N (as defined in Section 2.4.3) S-complex NEAs (Figure 2.12). All four asteroids with $Q > 3$ AU exhibit a (potential) 3- μm absorption feature. Six of the eight NEAs with a (potential) feature have aphelia greater than 2.06 AU, which means they enter the Main Belt (defined here as the location of the 4:1 resonance with Jupiter), compared to only one NEA out of four without a feature. Using aphelia to calculate the estimated minimum surface temperature on these asteroids shows that the NEAs with Band Shape Type 4 tend to achieve colder surface temperatures than the S-complex asteroids without a 3- μm feature. The temperature difference between the two populations is even larger when only considering S-complex asteroids with higher S/N spectra (see Table 2.6 for temperatures). Finally, the difference between aphelia and perihelia for Band Shape Type 4 NEAs is almost double that of the no-band higher S/N S-complex NEAs, and that difference is even larger for Ganymed and 2004 JN13. Eros is the only NEA with a (potential) feature whose aphelion-perihelion difference is less than the mean difference for the higher S/N S-complex asteroids without a feature.

2.6 Discussion

This survey has shown that OH/H₂O is prevalent, but not ubiquitous on NEAs and that NEAs with a 3- μm feature fall into four band shape groups, with some traits shared between all the NEAs with a (potential) 3- μm feature. If the OH/H₂O present on these surfaces was delivered via solar wind hydrogen implantation, OH/H₂O might be expected on all NEA surfaces because they are all impacted by the solar wind. As that is not the case, one or more factors must control the delivery and/or retention of OH/H₂O to/on nominally anhydrous and airless bodies.

2.6.1 Band Shape

The four band shape types seen in spectra of the eight NEAs with (potential) features

suggest different compositions and delivery/retention mechanisms, as seen in MBA surveys (e.g., Takir & Emery 2012; Rivkin 2010).

2.6.1.1 Type 1 – Wide Linear

As previously stated, to date, Band Shape Type 1 (Figure 2.8a) is seen on one NEA, 433 Eros (Figure 2.3a). Eros' feature is present at $> 2\sigma$, making it a definitive feature, and it has been detected multiple times. Eros is large, with $D \sim 17$ km, has a perihelion of 1.13 AU, is an S-type asteroid, and was sourced from either the Hungaria (46% probability) or ν_6 secular resonance region (45% probability) in the Main Belt (Granvik et al. 2018; Moskovitz et al. 2022). Eros also has the second smallest aphelion of the eight NEAs with a (potential) feature. The wide, linear, sharp feature possessed by Eros appears most similar to the sharp, Pallas-like band in Takir & Emery (2012) and Rivkin et al. (2019), and also strongly resembles the feature seen on the Moon. Based on the similarity in band shapes, it is likely that Eros and any future NEAs with Band Shape Type 1 have OH, rather than H_2O or some mixture, on their surfaces as determined by Takir & Emery (2012) for the Main Belt asteroids with sharp features. For the NEAs, we infer that the OH was likely delivered via solar wind hydrogen implantation, the mechanism that delivered OH/ H_2O to the Moon. The solar wind origin interpretation of some of the lunar OH is based on the temporal variations seen in the strength of the band as correlated to sub-solar position (e.g., Wöhler et al. 2017).

2.6.1.2 Type 2 – Narrow Linear

2004 JN13 (Figure 2.4a) is the only NEA exhibiting Band Shape Type 2 (Figure 2.8a). It is a moderately sized ($D = 2.4$ km) Sq-type NEA with the largest aphelion of any target studied by this survey. It is also unique in terms of source region, as it most likely escaped the Main Belt via the 5:2 mean motion resonance with Jupiter (55% probability) or possibly even from the

Jupiter Family Comet region (34% probability; Granvik et al. 2018; Moskovitz et al. 2022); neither of these regions are expected for many NEAs (Binzel et al. 2019). Though somewhat narrower, this feature is similar to that of Band Shape Type 1, indicating that, if real, OH rather than H₂O is likely present. Its perihelion is smaller than Eros', which in addition to its extreme aphelion and colder source region and therefore formation might explain why 2004 JN13 has a narrower 3- μ m band. However, without seeing the entirety of both this band and that of Eros, other explanations for the differences in band width are unclear.

2.6.1.3 Type 3 – Wide Bowl

Only one NEA in our sample, Ganymed (Figure 2.3b), exhibits a shallow, wide, bowl-like feature, which we label Band Shape Type 3 (Figure 2.8c). While no other NEAs exhibit this band shape type, two MBAs were studied using the same methods that do have very similar features: (4) Vesta and (349) Dembowska (Figure 2.13). Vesta, as mentioned previously, is known to have 3- μ m features heavily correlated to exogenous carbonaceous material impacts on its surface (e.g., DeSanctis et al. 2012; Reddy et al. 2012a; McCord et al. 2012). Our ground-based, disk-integrated spectrum of Vesta, like others, confirms the presence of hydrated material (Figure 2.13; e.g., Hasegawa et al. 2003). Additionally, the ground-based spectrum's 3- μ m band shape is nearly identical to the shapes shown by spectra c and d in DeSanctis et al.'s (2012) Fig. 2D. Dembowska, an R-type asteroid, shows a similar ground-based, disk-integrated spectrum. Given that R-types are spectrally similar to V-types (e.g., DeMeo et al. 2015), and that Ganymed is an Sr-type with an aphelion larger than either Vesta's or Dembowska's, it is likely that the 3- μ m feature on all three is caused by the same mechanism: exogenous carbonaceous material impacts. Additionally, Ganymed most likely escaped from the 3:1 mean motion resonance with Jupiter (62% probability; Granvik et al. 2018; Moskovitz et al. 2022), a region known to host

both carbonaceous and siliceous material (Walsh et al. 2013). Given the rough similarity between Ganymed's feature and the rounded feature described by Takir & Emery (2012), H₂O in addition to OH is likely present. However, additional H-bearing species may also be responsible for the features seen on Ganymed, as well as Vesta and Dembowska. Analysis of Dawn spectra of Ceres show that its feature is best matched by ammonia-bearing clays (e.g., DeSanctis et al. 2018), and analysis of Rosetta spectra of dark refractory material in the nucleus of 67P are best matched by ammonia-bearing salts (Poch et al. 2020). Potential carbonaceous contamination on Ganymed and other objects could therefore be N-H clays and/or salts from either a Ceres-like or 67P-like object. Further study is needed to determine if all R/V-type asteroids that have large aphelia and diameters are expected to contain exogenous carbonaceous material and a feature like Band Shape Type 3 or if there is something unique about these three asteroids.

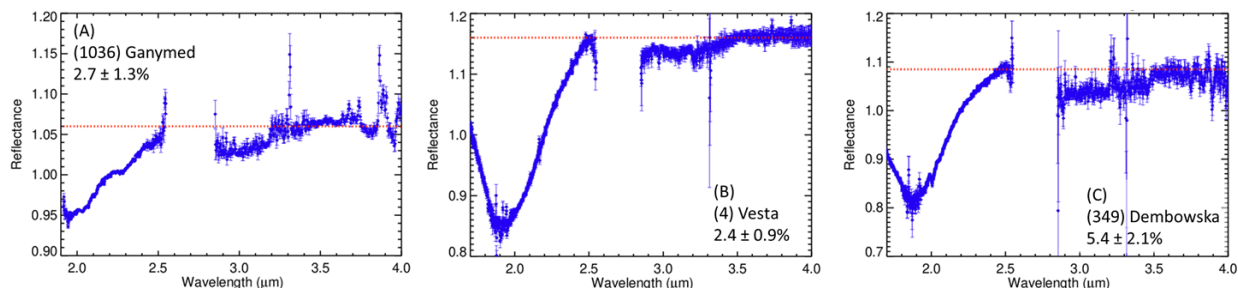


Figure 2.13: (A) 1036 Ganymed as observed on 19 Oct 2011. (B) 4 Vesta as observed on 2 Apr 2017. (C) 349 Dembowska as observed on 10 May 2019. All three asteroids have a similar band shape.

2.6.1.4 Type 4 – Narrow Bowl

Band shape Type 4 (Figure 2.8d) is categorized as a narrow bowl, with a shallowly sloped feature from 2.85 to ~ 3.0 μm that rapidly increases in reflectance from the band minimum to the reflected continuum between ~ 3.0 μm and ~ 3.05 μm . The five NEAs in this group are 2014 JO25, 1999 AP10, Florence, 1998 XB, and 2002 PZ39 (Figures 2.3c & 2.4), which are all 5 km or smaller and have perihelia less than 1.02 AU. The NEAs that exhibit Band

Shape Type 4 also have aphelia greater than 2.06 AU, which means they enter the Main Belt, except 1998 XB, which has the smallest aphelion of the eight NEAs with a (potential) feature of 1.23 AU. All five also were most likely sourced from the inner Main Belt, though 1999 AP10 has an even probability between the v_6 and 3:1 regions (46%). 1998 XB, 2002 PZ39, and 2014 JO25 most likely escaped from the v_6 region (68%, 89%, and 57% probabilities, respectively); Florence was sourced from the Hungaria (51% probability) or v_6 region (30% probability; Granvik et al. 2018; Moskovitz et al. 2022). 2002 PZ39 and 1998 XB are Q-types, Florence and 1999 AP10 are Sq-types, and 2014 JO25 is an Sr-type.

The bowl-like shape of the band likely indicates the presence of H₂O ice, possibly in addition to OH, as suggested in Takir & Emery (2012). Given the shallow nature of the band, OH/H₂O was likely either delivered to these objects via solar wind hydrogen implantation, just like for the NEAs with Band Shape Type 1, and/or through exogeneous carbonaceous material, like for Ganymed and Vesta. If the OH/H₂O was delivered via interactions with the solar wind, a different process must also be acting on the surfaces of these NEAs to cause the different band shape. If a process like recombinative desorption is occurring on the NEAs with this band shape, it could explain the bowl-like feature, which as mentioned above may be indicative of H₂O, rather than the linear one caused by only solar wind proton bombardment. However, given that all but one of the NEAs in this group enter the Main Asteroid Belt, the possibility for exogenous material is greater than for Eros, which does not interact with the Main Belt, so it is likely that asteroids with Band Shape Type 4 receive OH/H₂O through multiple mechanisms and from multiple sources.

2.6.2 Potential Driving Factors

The NEAs with (potential) 3- μ m absorption features share several similarities, both

within each band type group and all together, notably aphelion and spectral type, with weak trends evident in size, perihelion, orbital period, and albedo. Of the numerous other physical and orbital characteristics investigated, only the former two characteristics seem to control OH/H₂O delivery and/or retention, with the latter four appearing to have some degree of influence. However, other NEAs also exhibit one or two of the same characteristics but do not have a 3- μ m feature, implying none of these factors alone determines the presence of a 3- μ m absorption feature. Discussing these characteristics in terms of the band type groups clarifies their relationship to the delivery/retention process(es).

2.6.2.1 Composition and Albedo

All eight NEAs with a (potential) band are S-complex, therefore they all have regolith primarily composed of olivine and pyroxene. Seven of the eight also plot in the S(IV) ordinary chondrite “boot” on a Gaffey S subtypes plot (Figure 2.7). Within the S(IV) region, Florence plots in the LL ordinary chondrite sub-region, 1999 AP10 and 2014 JO25 plot in the H ordinary chondrite sub-region, and the other five plot in the L ordinary chondrite sub-region. Ganymed, the only one of the eight outside the S(IV) region, plots in the S(VI) region, which occurs between the ordinary chondrite “boot” and the basaltic achondrites (BA) region in terms of BAR. Other studies show that Ganymed can also plot in the S(IV)/H-chondrite sub-region (e.g., Thomas et al. 2014). As primitive achondrites often share the same region as H-chondrites on a Gaffey plot, the band I and II centers of 1999 AP10, 2014 JO25, and Ganymed were plotted and compared to the results found by Lucas et al., 2018; all three NEAs have BIIC values too high to be considered primitive achondrites. As Eros, the NEA with Band Shape Type 1, is an S-type, 2004 JN13 (Band Shape Type 2) is an Sq-type, Ganymed (Band Shape Type 3) is an S/Sr-type, and the NEAs with Band Shape Type 4 are a mix of Q-, Sq-, and Sr-types, exact spectral type

within the S-complex does not seem to influence band presence or shape type. The NEAs in the S-complex with no band are also a mix of the types mentioned. Additionally, calculated values for Fa and Fs content, as well as olivine ratio, show no trends with band depth or band shape type, as stated in Section 2.5.2. However, the weak association between higher albedo and the presence of a band, particularly a Type 4 feature, suggests a further compositional dependence that will be probed in future studies.

Several NEAs not in the S-complex but possessing similar size and perihelion to the NEAs with a (potential) band do not exhibit a 3- μ m absorption feature. The absence of 3- μ m features on the V-types studied implies that V-type NEAs do not tend to have OH/H₂O that was delivered via solar wind hydrogen implantation (or any of the other possible sources). This trend may be due to V-types' higher degree of silica saturation, as pyroxene, which dominates V-type surfaces, has a higher silicon-oxygen ratio than olivine, resulting in fewer relatively weak, ionic silica tetrahedron-to-metal bonds and more strong, covalent bonds between silica tetrahedra. The mechanical weathering step of the solar wind hydrogen implantation process appears to not be as efficient at breaking bonds and implanting hydrogen on V-types as on NEAs in the S-complex. Other studies have shown that irradiation and proton implantation experiments on olivine and pyroxene result in a greater spectral change on the olivine samples than the pyroxene samples (Yamada et al. 1999), suggesting that olivine is more easily changed than pyroxene by such processes. Only one of the three X-complex NEAs observed by this campaign has a higher S/N spectrum (153201) 2000 WO107) and, like the V-types, also does not have a 3- μ m feature. However, more observations of X-complex NEAs are needed to determine the prevalence of OH/H₂O across the X-complex population.

2.6.2.2 Aphelion and Orbital Period

Objects that enter the Main Belt are significantly more likely to have a 3- μ m band than those that do not, particularly when considering only S-complex NEAs. Six of the eight NEAs with a (potential) feature have aphelia large enough to carry them into the Main Belt. One of those six (Florence) has an aphelion greater than 2.5 AU and four (Ganymed, 2004 JN13, 1999 AP10, and 2014 JO25) have aphelia greater than 2.8 AU, indicating they travel into the middle and/or outer Main Belt as defined by the 3:1 and 5:2 Jupiter resonances, respectively.

Approximately 85% of S-complex NEAs in our sample with higher S/N spectra that enter the Main Belt have a (potential) 3- μ m feature (Figure 2.12), indicating that S-complex NEAs that enter the Main Belt are more likely to have OH/H₂O on their surfaces than S-complex NEAs that do not enter the Main Belt ($Q < 2.06$ AU). Additionally, 100% of higher S/N S-complex NEAs that enter the outer Main Belt have a 3- μ m absorption band. We observed four additional S-complex asteroids that enter the Main Belt, but the S/N of their spectra were too low to determine whether they exhibited a band (these are therefore not shown in Figure 2.10). Future observations of (5143) Heracles, (6063) Jason, (25916) 2001 CP44, and (143404) 2003 BD44, as well as other NEAs with large enough aphelia, will determine the robustness of this trend. The slight trend in orbital period noted previously is likely only a result of its dependence on aphelion, as no trend was discerned in orbital period prior to the discovery of the $Q > 2.06$ AU boundary in the data, though more observations are required to test this hypothesis.

Entering the Main Belt might aid in the delivery/retention of OH/H₂O in two ways. First, the likelihood that carbonaceous material will be delivered to an NEA's surface is significantly higher if that NEA spends time in the Main Belt, particularly the middle and outer Main Belt, as the middle and outer Main Belt contains far more carbonaceous material than near-Earth space or

the inner Main Belt do (Demeo et al. 2015). Second, a large aphelion means an NEA spends more of its orbit at a lower temperature, where OH/H₂O would be more stable and would then be more easily retained after delivery/creation. While a trend in band depth/shape with orbital phase is not apparent, further work is needed to determine if the observed features are stable or transient as the NEAs progress along their orbits. As discussed in section 2.5.2, the average estimated minimum surface temperature experienced by the NEAs exhibiting Band Shape Type 4 is lower than that of the S-complex NEAs that do not exhibit a feature. It is therefore likely that the time spent at a cooler temperature, as well as the availability of carbonaceous material, is a driver of OH/H₂O delivery and/or retention. A prediction from this apparent prevalence of 3- μ m bands on NEAs that enter the Main Belt is that Main Belt S-complex asteroids should show 3- μ m bands at a higher rate than NEAs. Nevertheless, two NEAs with 3- μ m features, Eros and 1998 XB, have aphelia less than 2.06 AU, implying that 3- μ m band presence is not wholly dependent on this supposed interaction with the Main Belt.

2.6.2.3 Diameter

Larger objects may be more likely to have a 3- μ m absorption feature than smaller objects. As stated in Section 2.5.2, the diameters of the NEAs with Band Shape Types 1 and 3 (Eros and Ganymed, respectively) are statistically significantly larger than the mean diameter of the NEAs with Band Shape Types 2 and 4 and the NEAs that do not have a 3- μ m feature. Of the five asteroids we observed with diameter ≥ 5 km, two possess a band, two do not exhibit a 3- μ m feature within the level of noise of the data (Ivar and Phaethon), and one has S/N that is too low to determine the presence of a feature (as defined in Section 2.4.3). For Phaethon, the absence of a 3- μ m band is likely due to its extreme surface temperatures near perihelion (Takir et al. 2020), and future observations of Ivar are required to see if its lack of feature is intrinsic or variable, as

seen by Rivkin et al. (2018) for Eros and Ganymed. For NEAs with $D < 5$ km, only six out of twenty-four exhibit a 3- μm band. Therefore, 50% of NEAs with $D > 5$ km exhibit a 3- μm feature versus 25% of NEAs with $D < 5$ km. However, while size seems to be important in the delivery and/or retention process, it does not control OH/H₂O completely, as the diameters of the NEAs with Band Shape Types 2 and 4 are statistically indistinguishable from those of NEAs with no 3- μm absorption feature.

Size could be important for several reasons. Larger asteroids present a larger projected area, so they are struck by more protons than smaller asteroids, even if the quantity per square meter is the same. Alternatively, and/or additionally, size may be important for OH/H₂O retention because larger asteroids have higher surface gravity so they may be able to hold on to implanted OH/H₂O more easily than small asteroids. Larger asteroids also tend to be older and have finer-grained regolith, whereas smaller asteroids are rockier (Gundlach & Blum 2013; Delbo et al., 2015). Both Eros' and Ganymed's published thermal inertias are fairly low (e.g., Mueller et al. 2007; Hinkle et al. 2022; Hanuš et al. 2015), suggesting fine-grained regoliths. The efficiency of the mechanical weathering process by which hydrogen is implanted may depend on grain size, as coarser and finer grains physically degrade at different speeds thereby influencing the efficiency of proton implantation, as discussed in Section 2.2.2. More research is required to calculate thermal inertias for more NEAs to determine the importance of grain size to OH/H₂O delivery and/or retention.

2.6.2.4 Perihelion

Lower perihelia may decrease the likelihood of an NEA containing OH/H₂O. The perihelia of NEAs with Types 1, 2, and 3 features are larger than the perihelia of NEAs without a feature (Figure 2.10), even though the mean perihelia of NEAs with a (potential) 3- μm

absorption feature are not statistically significantly different from those without. Nevertheless, the average perihelion of the Type 4 NEAs is indistinguishable from that of the higher S/N NEAs (Figure 2.10), meaning any trend in band depth presence with larger perihelion is not strong.

One reason perihelion distance could be related to the delivery and retention of OH/H₂O is the resulting higher maximum equilibrium and subsolar surface temperatures (Table 2.6).

OH/H₂O can dissociate at higher temperatures and therefore leave the surface. Evidence of this

Table 2.6: NEA and MBA Equilibrium and Subsolar Temperatures at Time of Observation, Perihelion, and Aphelion

	Object	η	Observation T_{Eq} (K)	Observation T_{SS} (K)	q T_{Eq} (K)	q T_{SS} (K)	Q T_{Eq} (K)	Q T_{SS} (K)
433	Eros	1	259	366	262	370	208	294
1036	Ganymed	1.12	233	330	243	344	134	189
1627	Ivar	1.3	236	333	249	352	163	231
1685	Toro	1.5	248	351	284	402	178	252
1981	Midas	1.3	254	359	329	465	151	214
3122	Florence	1.55	244	346	247	350	158	223
3200	Phaethon	1.6	246	348	671	949	162	229
5143	Heracles	1	257	363	430	608	155	219
6063	Jason	1	280	396	416	588	152	215
25916	2001 CP44	0.8	255	361	262	370	151	214
54789	2001 MZ7	1	226	319	227	321	169	239
66146	1998 TU3	1.4	239	338	400	566	237	335
66391	Moshup	1.6	246	347	552	781	237	335
68950	2002 QF15	1.3	258	364	310	439	216	306
85275	1994 LY	1.6	238	337	245	347	152	215
96590	1998 XB	1.2	244	345	336	475	233	329
143404	2003 BD44	1	261	369	315	445	156	221
144332	2004 DV24	1.3	259	367	260	367	193	273
153201	2000 WO107	1.05	273	386	622	880	218	309
159402	1999 AP10	1.7	232	329	239	338	124	176
163373	2002 PZ39	0.8	290	411	357	505	194	274
163696	2003 EB50	1.65	233	329	276	390	156	220
194126	2001 SG276	1.2	254	359	255	361	199	281
214088	2004 JN13	0.98	262	370	300	424	127	179
285944	2001 RZ11	2.5	167	236	209	295	120	169
332446	2008 AF4	1.6	247	349	274	388	177	250
357439	2004 BL86	1.4	252	357	264	374	173	244
454177	2013 GJ35	1.35	234	332	249	352	146	206
	2014 JO25	0.95	274	387	575	813	143	202
4	Vesta	0.81	183	259	196	277	179	253
349	Dembowska	0.9	158	223	173	244	157	222

process was potentially seen on the Moon, as the lunar 3- μm band depth was found by some to be shallowest at local noon and deepest in the morning and evening (McCord et al. 2011), though new interpretations have since been published (Ruiz et al. 2020; see Section 2.2.2). As mentioned above, Phaethon’s perihelion of 0.14 AU leads to a surface temperature of over 1000 K (Takir et al. 2020), which likely means that OH/H₂O is not stable on its surface, or at least not

near perihelion.

On the other hand, some NEAs with Band Shape Type 4 have smaller perihelia, so clearly a small perihelion does not preclude the potential for a 3- μm absorption feature. Objects closer to the Sun experience a higher flux of solar wind protons (Nicolaou et al. 2020) and might therefore be expected to experience more hydrogen implantation. However, at small enough perihelia, such as the case for 2014 JO25 and Phaethon, the surface temperature would be high enough to cause some degree of dehydration (Springmann et al. 2019), so even if OH and/or H₂O were being created, it might not be retained. On the other hand, a process such as recombinative desorption could allow for the formation of H₂O even on surfaces with relatively high maximum temperatures, such as experienced by those NEAs with Band Shape Type 4 (Orlando et al. 2018). Recombinative desorption is a process by which two -OH groups in close proximity thermally react to form H₂O in minerals that have saturated -OH terminal sites and defects (Orlando et al. 2018). Temperatures above 450 K are required for the process to occur; the maximum equilibrium and subsolar temperature on 2014 JO25 are above that threshold, though 1999 AP10 and Florence do not reach such a temperature, regardless of considering the whole-body equilibrium temperature or the peak temperature at the subsolar point (Table 2.6). However, meteorite impacts can raise the surface temperature of the affected area enough to make recombinative desorption possible (Orlando et al. 2018), and micrometeorite impacts are more likely closer to the Sun than at larger heliocentric distances, even within the Main Belt (Grün & Zook 1980; Pokorný et al. 2021). Perihelion, and maximum surface temperature, therefore seems to be relevant to both OH/H₂O delivery/retention and exact volatile composition and band shape.

2.6.3 S-Complex Non-Detections

The bulk of this discussion has focused on the NEAs that have or potentially have a 3- μm

feature. However, when only considering the asteroids with band depth errors less than $\sim 5\%$ and removing any NEAs not in the S-complex from this list, we are left with only five S-complex NEAs with higher S/N spectra that do not have a $3\text{-}\mu\text{m}$ feature: (66391) Moshup, (66146) 1998 TU3, (1685) Toro, (1627) Ivar, and (194126) 2001 SG276. These five objects are indistinguishable from the eight with a (potential) feature in terms of composition, diameter, and perihelion. The question then becomes why these five S-complex NEAs do not have a feature, rather than why the eight S-complex asteroids with higher S/N do.

The most likely explanation for the lack of a feature on these five objects is their relatively low aphelia. Four of the five NEAs do not enter the Main Belt, and the remaining object, Ivar, does not enter the outer belt. Considering $\sim 85\%$ of higher S/N S-complex NEAs that enter the Main Belt have a $3\text{-}\mu\text{m}$ absorption feature and $\sim 67\%$ of higher S/N S-complex NEAs that do not enter the Main Belt do not have a $3\text{-}\mu\text{m}$ absorption feature, entering or not entering the Main Belt appears to be a primary driver on the presence of OH/H₂O on NEAs. It will be interesting to re-observe Ivar at different orbital and rotational phases to see if Ivar's band depth varies, as Rivkin et al. (2018) showed for Eros and Ganymed, or if its lack of feature is inherent. If the latter is true, future observations will help elucidate other drivers of OH/H₂O delivery and/or retention.

2.6.4 Observational Bias

Though we observed every NEA bright enough to search for a $3\text{-}\mu\text{m}$ feature over the course of five years (when the weather cooperated), observational bias still exists. Perhaps most obviously, given that we had a brightness requirement and we sampled known NEAs, which from the ground are discovered based on visible detections, our sample is biased to higher albedo objects. Our targets sample a wide range of perihelia, from 0.14 AU (3200 Phaethon) to 1.3 AU

(Figure 2.6), the limit that defines a near-Earth asteroid. The mode of our perihelia is ~ 1 AU, which matches the overall NEA population (Binzel et al. 2015; Valdes 2019), but our distribution is different. According to CNEOS cumulative discovery statistics, $\sim 8\%$ of NEAs are Atens ($q < 1.0$ AU), $\sim 56\%$ are Apollos ($1.0 < q < 1.017$ AU), and $\sim 36\%$ are Amors ($1.017 < q < 1.3$ AU). Our NEAs are $\sim 59\%$ Atens, $\sim 7\%$ Apollos, and $\sim 34\%$ Amors, so our sample is overrepresented in Atens and underrepresented in Apollos. The aphelia distribution of our targets generally matches that of the overall NEA population, as aphelia are fairly uniformly distributed between 1 AU and ~ 4.5 AU, with a small population of NEAs possessing aphelia up to 6 AU (Valdes 2019). As for diameter, only $\sim 4\%$ of all known NEAs are larger than 1 km and only $\sim 20\%$ of those are larger than or equal to ~ 5 km in diameter. In contrast, 82% of the NEAs observed in this study are larger than 1 km in diameter and five of those are larger than or equal to 5 km. We therefore have an observational bias because our study only samples NEAs with diameters well outside the mean. In terms of spectral type, the general NEA population is $\sim 67\%$ S-complex, $\sim 14\%$ C-complex, $\sim 8\%$ X-complex, and $\sim 4\%$ V-types (Binzel et al. 2015). We primarily observed S-complex NEAs ($\sim 67\%$), with five V-types ($\sim 18\%$), three X-complex ($\sim 11\%$), and only one C-complex ($\sim 4\%$; Figure 2.6). We therefore have little apparent observational bias for S- and X-complex NEAs, though the X-complex is compositionally diverse, but we oversampled V-types and undersampled C-complex NEAs. On a macroscale, our target list is relatively representative of the NEA population as a whole, except in regard to albedo and diameter, and we deviate slightly from the NEA population distribution in terms of perihelion. Given that we are generally not strongly biased in aphelion and composition and considering that aphelion and composition seem to be more important to the delivery and/or retention of OH/H₂O than albedo, diameter and perihelion, the observational biases in our sample are not expected to strongly

affect our conclusions, though these biases might imply OH/H₂O is not as prevalent in near-Earth space as our findings suggest. Reducing our observational bias through future observations will improve our understanding of the statistics of 3- μ m bands on NEAs and clarify the trends seen by this study.

2.7 Summary and Conclusions

We conducted a survey of near-Earth asteroids to determine the prevalence of OH/H₂O in near-Earth space. These nominally anhydrous inner Solar System bodies have been subjected to various mechanisms and processes that implant OH/H₂O, such as carbonaceous/cometary material impacts and solar wind hydrogen implantation. We presented here 33 observations of 29 NEAs and two observations of Main Belt Asteroids using NASA's IRTF SpeX near-infrared spectrometer to further understand the mechanisms and processes involved in OH/H₂O delivery and retention, and determine which factors are most important in controlling the presence of a 3- μ m absorption feature.

Of those 29 NEAs, observations of 19 produced high enough S/N spectra to determine the presence or lack thereof of an absorption feature in the 3- μ m spectral region. Eight of those exhibit a band to either 1- or 2 σ : (433) Eros, (214088) 2004 JN13, (1036) Ganymed, 2014 JO25, (159402) 1999 AP10, (3122) Florence, (96590) 1998 XB, and (163373) 2002 PZ39. The remaining eleven are featureless at the few % level. We also identified four band shape types. Eros possesses a wide linearly increasing feature similar to the deeper feature seen on (2) Pallas. 2004 JN13 has a similar feature, but it is much narrower. Both NEAs (Band Shape Types 1 and 2) likely contain OH on their surface rather than H₂O or some mixture, based on band shape, which was delivered via solar wind hydrogen implantation. Ganymed exhibits a wide, shallow bowl-like feature, likely indicating a mix of OH and H₂O, that is nearly identical in shape to our

ground-based observation of (4) Vesta and (349) Dembowska. As Vesta's hydration is known to have an exogeneous carbonaceous material source, Ganymed's OH/H₂O was likely delivered via the same mechanism. The remaining five NEAs exhibit Band Shape Type 4, a narrow bowl-like feature, also likely an indication of a mix of OH and H₂O; however, their shape differs enough from Ganymed's to suggest that the source of their OH/H₂O may be different. A combination of processes likely delivered this volatile, such as solar wind hydrogen implantation in addition to recombinative desorption.

Given that all eight NEAs with a (potential) 3- μ m feature belong to the S-complex and that six of them have aphelia large enough to enter the Main Belt, composition and aphelion appear to be the two most significant driving factors in OH/H₂O delivery and/or retention. V-types' pyroxene-rich composition may not be conducive to OH/H₂O formation/retention. Minor trends with diameter, perihelion, orbital period, and albedo were also identified, though more data is required to determine their importance and untangle competing effects. Our study not only determined that nominally anhydrous, inner Solar System bodies, and therefore near-Earth space in general, contain more OH/H₂O than previously expected, we also found strong trends that can help predict which NEAs that have not yet been observed might contain OH/H₂O on their surfaces. In particular, S-complex NEAs that enter the Main Belt appear more likely to have a 3- μ m feature than not, and future observations will further investigate the reason for this trend.

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3. A Case Study for 3- μ m Band Depth Variations: (433) Eros, (1036) Ganymed, & (3122) Florence

Abstract

Near-Earth Asteroids (NEAs) are excellent laboratories for processes that affect the surfaces of airless bodies. Most NEAs were not expected to contain OH/H₂O on their surfaces because they formed in the anhydrous regions of the Solar System and their surface temperatures are high enough to remove these volatiles. However, a 3- μ m feature typically indicative of OH/H₂O was identified on other seemingly dry bodies in the inner Solar System, such as the Moon and Vesta, and more recently on the NEAs (433) Eros, (1036) Ganymed, and (3122) Florence. Possible sources for OH/H₂O on these bodies include carbonaceous chondrite impacts or interactions with protons implanted by solar wind. We investigated the causes of band depth and shape variations on NEAs by comparing new observations of Eros and Ganymed to those previously published and conducting a rotationally-resolved spectral study on Florence. All spectra discussed were collected by SpeX on NASA's IRTF using the LXD_short (1.67-4.2 μ m) mode to characterize the 3- μ m region. Some observations also used the prism (0.7-2.52 μ m) mode to characterize asteroid spectral type and investigate silicate composition dependencies. All three asteroids possess exogenously sourced OH/H₂O and have spectra that show potential spatial correlations in band depth or shape. Eros' band is slightly wider at the poles than at lower sub-observer latitudes, possibly due to its sunward polar orientation. Ganymed's asymmetrically parabolic trend in band depth with sub-solar longitude and negative trend in band depth with band I center suggest a magnesium-enriched carbonaceous or cometary impactor that struck the surface around 0° relative longitude. Florence's total hydrogen concentration remains stable across the surface even as the OH-to-H₂O ratio changes as the asteroid rotates. These three

examples suggest that non-native OH/H₂O on other bodies will likely also be spatially dependent, regardless of delivery mechanism.

3.1 Introduction

As remnants of primordial planetary building blocks, asteroids contain the key to understanding Solar System history and evolution. In particular, studying volatiles such as hydroxide and water (OH/H₂O) and their current prevalence in the inner Solar System and near-Earth space can elucidate the historical distribution of such materials and therefore the source of terrestrial water, a necessary component of life (e.g., Morbidelli et al. 2000). Numerous studies (e.g., Sunshine et al. 2009, Pieters et al. 2009, Clark 2009, De Sanctis et al. 2012, Rivkin et al. 2018, McGraw et al. 2022) have proved the existence of OH/H₂O on bodies within the inner Solar System (i.e., within Jupiter's 3:1 mean motion resonance), showing that OH/H₂O is more prevalent in near-Earth space than previously believed (e.g., Grossman & Larimer 1974, Muralidharan et al. 2008).

While knowing the extent to which OH/H₂O is present in near-Earth space is vital, studying the distributions of such volatiles in detail on a select few targets can elucidate the delivery, retention, and/or creation mechanisms experienced on the surface. For instance, the numerous studies on two particular inner Solar System bodies, the Moon and (4) Vesta, showed unexpected widespread evidence of hydration across the surface of each body (e.g., Sunshine et al. 2009; Pieters et al. 2009; Clark 2009; Simon et al. 2019; Ruiz et al. 2020; Honniball et al. 2021; De Sanctis et al. 2012; Prettyman et al. 2012; McCord et al. 2012; Reddy et al. 2012; De Sanctis et al. 2013). These studies, however, clearly indicated a different delivery mechanism was responsible for the hydration seen on each object. The global, diurnally varying absorption feature indicative of OH/H₂O on the Moon is likely due to the implantation of hydrogen ions

sourced from the solar wind (e.g., Sunshine et al. 2009), though recent studies suggest additional processes may be involved (e.g., Burke et al. 2011; Schaible & Baragiola 2014; Orlando et al. 2018; Zhu et al. 2019) or that poor thermal modelling is responsible for the apparent diurnal component (e.g., Ruiz et al. 2020). However, the M³ data from Chandrayaan-1 used to refute the diurnal variations (Ruiz et al. 2020) only extends to 2.95 μm (Pieters et al. 2009), so the thermal model is fit to the absorption feature, thereby assuming the band depth and shape. Datasets that include the entire hydration band and/or wavelengths longward of the band, such as those from Deep Impact (Sunshine et al. 2009) and this study, allow the hydration band depth and shape to be generally independent of the thermal model, as the model fits the thermal tail by assuming an absence of absorption features longward of the band. In comparison, studies of the hydration feature on Vesta showed a strong correlation between OH/H₂O signatures and low albedo regions, suggesting exogenous carbonaceous material as the source, rather than solar wind proton implantation as on the Moon (e.g., McCord et al. 2012; De Sanctis et al. 2012). Understanding the processes responsible for a 3- μm feature on a particular target can further constrain those processes on targets for which such a study is not yet possible. While spacecraft missions are obviously ideal for such work, multiple ground-based observations of the same target, such as a near-Earth asteroid (NEA), can also address temporal and spatial distributions of these materials in order to determine how OH and/or H₂O is delivered.

Prior to the discovery of OH/H₂O at all latitudes on the Moon (Sunshine et al. 2009; Pieters et al. 2009; Clark 2009), airless inner Solar System bodies were assumed to be generally devoid of surficial molecular OH/H₂O, due in part to forming within the frost line where water and hydroxide could not condense. Additionally, the lack of an atmosphere suggests secondary OH/H₂O would be unstable on ordinary-chondrite-like, i.e., not OH-bearing, surfaces (e.g.,

Muralidharan et al. 2008). This discovery, along with that on Vesta and others of 3- μ m features on inner Solar System bodies (e.g., Rivkin et al., 2018), motivated a near-infrared survey of every NEA bright enough to observe in the 2-4- μ m spectral region to constrain the OH/H₂O budget of the inner Solar System (McGraw et al. 2022).

The McGraw et al. (2022) survey sampled a wide variety of spectral types (S- and X-Complex and V-types), and only objects in the S-complex exhibited a 3- μ m feature. Of the thirteen S-complex NEAs with high signal-to-noise ratio (S/N) spectra, eight possessed an absorption feature, three with a band depth greater than the 2σ error and five with a depth greater than the 1σ error. Those eight objects exhibited four different band shapes, which were used to deduce the volatile composition (hydroxide, water, or a mix) and infer delivery mechanism, similar to other studies (e.g., Rivkin 2010; Takir & Emery 2012; Rivkin et al. 2019). Two of the groups, described as wide linear and narrow linear, likely indicate a purely hydroxide volatile composition that was delivered via solar wind hydrogen implantation (e.g., Zellner et al. 1966; Starukhina 2001), as suggested for the Moon (Sunshine et al. 2009; Pieters et al. 2009; Clark 2009). Another band shape, described as a wide bowl, is also seen on ground-based spectra of Vesta (e.g., Hasegawa et al. 2003; McGraw et al. 2022) and in some spectra collected by Dawn (De Sanctis et al. 2012). This wide bowl feature is therefore likely indicative of exogeneous carbonaceous material and is caused by a mixture of hydroxide and water, with the potential addition of ammonia-bearing species (De Sanctis et al. 2018; Poch et al. 2020). The final band shape seen by McGraw et al. (2022) is a narrow bowl, which is again likely indicative of a hydroxide-water mixture, delivered either via exogeneous carbonaceous material as on Vesta or solar wind-implanted protons altered by recombinative desorption (Orlando et al. 2018).

The two largest NEAs, (433) Eros and (1036) Ganymed, have been observed numerous times in the 2-4- μ m spectral region (e.g., Rivkin et al. 2018; McGraw et al. 2022). Eros, an S-type asteroid, exhibited a wide linear feature in the McGraw et al. (2022) spectrum so is believed to have surficial OH that was delivered via solar wind hydrogen implantation. Ganymed, an Sr-type asteroid, exhibited a wide bowl feature in the McGraw et al. (2022) spectrum so is believed to have a mix of OH and H₂O, potentially along with -NH, that was delivered via carbonaceous material impacts. Rivkin et al. (2018) showed a wide variety in the band depths and shapes present on these two asteroids, with depths ranging from $0.0 \pm 2.0\%$ to $5.0 \pm 2.7\%$ for Eros and $0.0 \pm 1.5\%$ to $6.2 \pm 2.1\%$ for Ganymed. They found a potential band depth dependence on surface features for Eros, and a potential negative trend in the 3.1 μ m-to-2.95 μ m reflectance ratio with heliocentric distance for both asteroids.

Further study of an object that experienced the third volatile delivery mechanism discussed in McGraw et al. (2022) will also enable greater understanding of near-Earth space volatiles. (3122) Florence, an Sq-type asteroid, exhibited a narrow bowl-like band in the average spectrum shown by McGraw et al. (2022). Florence has a much faster rotation rate than Eros and Ganymed (Table 3.1), allowing for a rotationally resolved study, which will help clarify the volatile delivery mechanism and therefore our understanding of the OH/H₂O budget of near-Earth space.

Table 3.1: NEA Physical and Orbital Characteristics

Object		D ^a (km)	Tax. ^b	q ^a (au)	Q ^a (au)	Orb. Per. ^a (Yrs)	Rot. Per. ^a (hrs)	Albedo ^a
433	Eros	16.8	S	1.13	1.78	1.76	5.27	0.25
1036	Ganymed	37.7	S/Sr	1.24	4.09	4.35	10.30	0.24
3122	Florence	4.9	Sq	1.02	2.52	2.35	2.36	0.23

^aValues from JPL Horizons

^bValues from McGraw et al. (2022)

3.2 Methods

3.2.1 Data Acquisition and Processing

The spectra discussed herein (Table 3.2; tables 1-3 in Rivkin et al. 2018), including those published in Rivkin et al. (2018), were collected using the near-infrared spectrograph SpeX on NASA’s IRTF (Rayner et al. 2003). We used the long-wavelength cross-dispersed short mode (LXD_short; 1.67-4.2 μm) to study the 3- μm feature indicative of OH/H₂O and the shorter wavelength prism mode (0.7-2.5 μm) to conduct mineralogical determinations. Both gratings were used with a 0.8x15” slit. As described in McGraw et al. (2022), during the course of which the spectra of Eros, Ganymed, and Florence used in this work were collected, targets were tracked using the V-band filter in the MIT Optical Rapid Imaging System (MORIS), and the telescope alternated between a selected local standard star and the asteroid every 10 to 30 minutes to ensure adequate atmospheric removal. Nodding within the slit enabled background sky emission subtraction.

A variety of IDL-based software packages were used to process the collected data, primarily the Spextool package written for use with SpeX (Cushing et al. 2004; Vacca et al. 2003). We used this package to flat field correct, extract, and wavelength-calibrate the raw data, before using it to remove atmospheric absorptions in the LXD data. An ATRAN-based code (MacLennan 2019) was used to atmospherically correct the prism data. The resulting spectral frames were then combined using the standard error robust mean statistical method and the LXD orders were merged to create the final spectrum. Spectra of Eros and Ganymed are composed of all frames taken in one night of observing (Table 3.2). The spectra for Florence were all taken in a single night, with each spectrum representing one set of asteroid frames that was bookended by star frames. As mentioned in section 2.2, Florence has a relatively fast

rotation period of 2.358 hr (Table 3.1), so one night of observing covered almost one and a half complete rotations of Florence. Each spectrum represents approximately a quarter of the surface area, as Florence's spin pole is nearly perpendicular to the ecliptic and its shape is roughly spheroidal (Franco et al. 2018), with the first and last spectra having some overlap in surface coverage.

Table 3.2: Observing Parameters & Conditions of NEAs Observed in this Study

Date (UT)	V mag ^a	LXD Midtime (UT)	LXD Int. Time (s) x Images	Prism Midtime (UT)	Prism Int. Time (s) x Images	Standard Star	Solar Dist. ^a (AU)	Earth Dist. ^a (AU)	Phase Angle ^a	Weather ^b (Seeing)
(433) Eros										
1-Sep-2009	11.1	11:03	15 x 60	12:09	15 x 8	SAO 127422	1.689	0.694	9.04	Cl (1.5")
28-Jan-2012	7.8	13:18	20 x 80	12:20	1(8) ^c x 8	HD 89909	1.136	0.179	29.69	Cl (0.5")
21-Aug-2016	12.0	10:03	30 x 52	8:34	20 x 16	HD 208298	1.732	0.728	6.33	Cl, H (0.6")
28-Aug-2016	11.3	9:30	30 x 160	--	--	HD 206559	1.721	0.725	8.67	Cl (0.6")
13-Dec-2018	8.7	12:12	30 x 64	13:21	4 x 12	BD+58 681	1.193	0.255	31.24	Cl (0.5")
4-Jan-2019	8.2	9:03	30 x 128	6:12	3 x 8	HD 28005	1.153	0.214	34.07	Cl (0.5")
25-Mar-2019	10.9	7:34	15(2) ^c x 128	9:39	30x8; 60x8	HD 61809	1.197	0.387	51.14	PaC (1.0")
18-May-2019	12.4	7:14	15(2) ^c x 96	8:39	30x2;40x8	SAO 155741	1.354	0.724	47.12	Cl, H (1.0")
(1036) Ganymed										
10-Jun-2011	11.4	14:00	15(2) ^c x 150	11:44	60x8; 30x8; 15x8	HD 197207	1.535	0.890	39.18	MC (0.8")
4-Jul-2011	11.0	11:54	20 x 140	10:34	10 x 16	HD 204570	1.404	0.752	44.66	Cl (1.6")
26-Sep-2011	9.2	11:50	20 x 80	10:27	2(5) ^c x 16	HD 232456	1.271	0.392	39.90	Cl (0.6")
19-Oct-2011	8.5	10:04	20 x 240	7:51	1(10) ^c x 16	HD 12846	1.349	0.365	12.82	Ci (0.4")
31-Oct-2020	13.2	14:05	30 x 188	11:26	40x16; 80x16	HD 59474	2.131	1.696	27.15	MCl, Ci, W (0.7")
9-Dec-2020	13.1	12:29	30 x 160	14:48	80 x 32	HD 55713	2.445	1.626	15.72	Cl (0.5")
(3122) Florence										
5-Aug-2010	14.2	13:50	15(4) ^c x 56	--	--	SA 115-271	1.071	0.344	71.33	Ci (0.7")
3-Sep-2017 Avg	9.0	8:58	15(2) ^c x 116	6:32	8 x 8	HD 197076	1.046	0.049	39.45	Cl (0.9")
3-Sep-2017 A	8.99	7:34	15(2) ^c x 32	--	--	HD 197076	1.047	0.049	39.00	Cl (0.9")
3-Sep-2017 B	9.00	8:30	15(2) ^c x 28	--	--	HD 197076	1.046	0.049	39.30	Cl (0.9")
3-Sep-2017 C	9.01	9:28	15(2) ^c x 28	--	--	HD 197076	1.046	0.049	39.60	Cl (0.9")
3-Sep-2017 D	9.02	10:24	15(2) ^c x 28	--	--	HD 197076	1.046	0.050	39.89	Cl (0.7")

^a Values from JPL Horizons

^b (M)Cl-(mostly) clear, Ci-cirrus, PC-partly cloudy, MC-mostly cloudy, PaC-patchy clouds, (V)W-(very) windy, F-foggy, H-humid

^c Parenthetical represents number of coadds. All other observations used 1 coadd.

Table 3.3: Sub-Observer and Sub-Solar Coordinates at Time of Observation

Date (UT)	Sub-Observer Latitude	Sub-Observer Longitude	Sub-Solar Latitude	Sub-Solar Longitude
(433) Eros^a				
McGraw et al. Observations				
1-Sep-2009	-86	121	-85	106
28-Jan-2012	86	33	78	28
21-Aug-2016	-84	90	-83	81
28-Aug-2016	-83	13	-84	3
13-Dec-2018	-81	189	-79	225
4-Jan-2019	-82	47	-58	69
25-Mar-2019	66	101	87	74
18-May-2019	85	45	89	209
Rivkin et al. Observations				
27-Aug-2011	-85	24	-90	124
30-Oct-2011 A	-64	347	-85	8
30-Oct-2011 B	-78	35	-85	57
6-Dec-2011	81	314	-76	342
25-Jan-2012	86	53	76	53
1-May-2012	86	274	89	57
4-Jun-2012	88	262	87	39
3-Jul-2012	89	357	84	42
(1036) Ganymed^b				
McGraw et al. Observations				
10-Jun-2011	53	288	24	323
4-Jul-2011	66	32	29	73
26-Sep-2011	49	145	22	183
19-Oct-2011	23	28	14	38
31-Oct-2020	-29	329	-17	356
9-Dec-2020	-37	117	-22	128
Rivkin et al. Observations				
23-Jun-2011	60	170	27	207
5-Jul-2011	66	161	29	202
27-Aug-2011	67	32	30	97
28-Aug-2011	66	255	30	319
30-Oct-2011	10	165	10	164
6-Dec-2011	-11	225	-2	200
30-Jan-2012	-14	277	-14	246
(3122) Florence^c				
3-Sep-2017 A	--	0	--	--
3-Sep-2017 B	--	143	--	--
3-Sep-2017 C	--	290	--	--
3-Sep-2017 D	--	73	--	--

^a Values from JPL Horizons^b Values from DAMIT (<https://astro.troja.mff.cuni.cz/projects/damit/>; Ďurech et al. 2010; Viikinkoski et al. 2017)^c Values relative to starting observation

3.2.2 Thermal Tail Removal

The LXD spectrum contains a significant thermal component longward of approximately 2.8 μm , depending on surface temperature. The thermal tail must be removed in order to leave only the reflected component before band depth analyses can be completed. We used a thermal model based on the near-Earth asteroid thermal model (NEATM; Harris 1998) to remove the thermal tail, during the course of which the reflected continuum is extrapolated from the shorter wavelengths to approximate the expected reflectance-only linear spectrum at longer wavelengths. The beaming parameter and the continuum slope and vertical position were iteratively varied to produce the best-fit continuum, and therefore the best-fit thermal model, resulting in the longer wavelength data lying along the continuum. The band depth was then calculated as the difference between the continuum and reflectance at a given wavelength. The

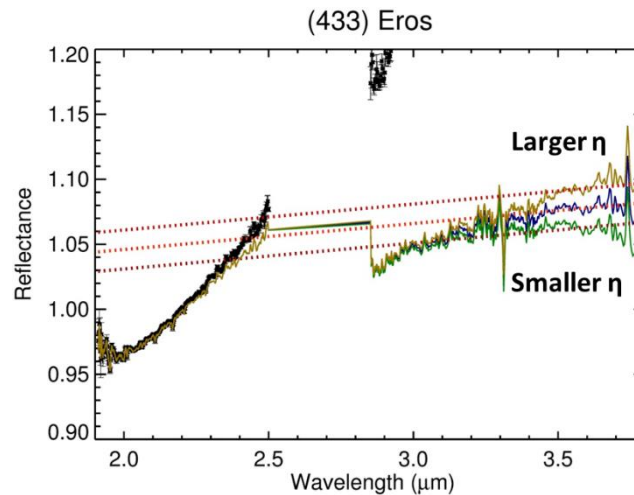


Figure 3.1: Example spectrum of (433) Eros showing the effect of continuum placement and beaming parameter selection on the 3- μm band. Black data points represent spectrum before thermal tail removal (i.e., reflected and thermal components). Yellow, blue, and green data represent spectra after thermal tail removal (i.e., only reflected component), and red dashed lines represent reflected continua. Reflected continua with too high of reflectance values at 2.45 μm and/or too low of beaming parameters result in an undercorrected spectrum (yellow line). Reflected continua with too low of reflectance values at 2.45 μm and/or too high of beaming parameters result in an overcorrected spectrum (green line). Modified from Wigton (2015).

error in band depth is calculated by including the point-to-point spread in the data, propagation of uncertainties from the spectrum, and subjectivity of continuum placement. A method similar to that described in McGraw et al. (2022) was used to verify the chosen continuum slopes and associated errors. Though continuum placement and beaming parameter can significantly affect the longer wavelengths, the 3- μm band remains relatively unchanged (Figure 3.1), though band depth is dependent on the selected continuum.

The data published in Rivkin et al. (2018) were similarly thermally corrected using a modified standard thermal model (Lebofsky et al. 1986) that was used in previous work (e.g., Rivkin et al. 2006, 2013). However, the reflected continuum was selected using a different method than described above. For both Eros and Ganymed, Rivkin et al. (2018) fixed the continuum value at 3.8 μm , which was estimated from previously published studies of these two objects and meteorite data (Trilling et al. 2010; Mainzer et al. 2011). They then used reflectance ratios of 3.8 μm to 2.45 μm equal to 1.05 and 1.10 for Eros and Ganymed, respectively, to set the continuum value at 2.45 μm and therefore determine the continuum slope (Rivkin et al. 2018).

3.2.3 Band Parameter Analysis

3.2.3.1 Prism Bands

The 1- and 2- μm absorption features (BI and BII, respectively) for each observation with prism data were characterized by the band center wavelengths (BIC and BIIC) and band-area ratio (BAR). We used the Band Analysis Routine for Asteroids (BAR-Ast; MacLennan 2019), which is based on the Spectral Analysis Routine for Asteroids (SARA; Lindsay et al. 2015) to calculate these parameters and their uncertainties. As the relations between band parameters and mineralogy were derived from spectra of meteorite samples (e.g., Dunn et al. 2010), several

corrections for temperature, instrument wavelength range, and S/N are needed to use such equations on asteroid spectra. Numerous studies have determined the proper adjustments needed for these corrections for S-complex asteroids (e.g., Sanchez et al. 2012; Lindsay et al. 2016; Sanchez et al. 2020). The equations published by Sanchez et al. (2020) were used on this dataset.

3.2.3.2 OH/H₂O Band

The OH/H₂O band is characterized at five wavelengths (2.9 μm , 2.95 μm , 3.0 μm , 3.05 μm , and 3.1 μm) to assess band presence and shape. The band depth (BD) at each of these wavelengths is calculated, after thermal tail removal and binning by a factor of 9 to approximate the slit width, by taking the robust mean of the data points in a 0.05- μm band width centered on the wavelength of interest for both the reflected continuum (RC) and the reflectance spectrum (RB) and using the formula, $BD = \frac{RC-RB}{RC} * 100$. The error in band depth was calculated using standard error propagation techniques and adding in quadrature the error in reflected continuum choice (see Section 3.3.2). Bands with depths greater than the 2σ -error are considered definitively present and bands with depths greater than the 1σ -error are considered potentially present. Rivkin et al. (2018) published band depths at 2.95 μm and 3.1 μm and used the reflectance ratio between these two wavelengths ($R_{3.1}/R_{2.95}$) as an evaluation of band shape. We also calculated this reflectance ratio to make comparisons.

3.2.4 Integrating Rivkin et al. 2018 Dataset

Given the differences in processing and thermal modelling between the Rivkin et al. (2018) data and the newly collected data published herein, some re-working of the Rivkin et al. (2018) dataset was required to ensure even comparisons. We ran the processed and extracted data from Rivkin et al. (2018) through the same thermal model used for our other spectra, as

well as chose reflected continua using the methods described in section 3.2.2. Most of the resulting band depths were within 1σ of those published by Rivkin et al. (2018). The band depths that varied from those previously published can be explained by substantial differences in continuum placement and/or slope.

We also re-extracted and re-processed three of the observations of Ganymed (10 June, 4 July, and 28 August 2011), starting from the raw data, to ensure that differences in the procedures used by Rivkin et al. (2018) and those used in this study prior to thermal tail removal produced negligible variations in the final spectra and depths. While some minor differences in band shape were evident between the two versions, likely a result of different continuum placements, the band depths were within 1σ of each other, confirming the different extraction and processing procedures produce negligibly different results. For these Rivkin et al. observations, the spectra extracted and processed from the raw data are reported here.

3.3 Results

3.3.1 (433) Eros

We made eight observations of Eros (Tables 3.2 & 3.3 and Figure 3.2), two of which (1 September 2009 and 28 January 2012) were previously published by Wigton (2015) and were re-extracted to ensure equal comparison with subsequently collected data. We obtained prism spectra for all but one observation, 28 August 2016 (Figure 3.3). We used $2.9\ \mu\text{m}$ as the wavelength to classify the presence of a band, as this wavelength is the closest reliable point in the spectrum to the atmosphere-obscured band center ($\sim 2.7\ \mu\text{m}$). Two observations exhibit a band depth greater than or equal to the 2σ error, four exhibit a band depth greater than the 1σ error (but less than the 2σ error), and two do not have a band. Using a histogram of S/N values for all Eros spectra to find a break point between higher and lower S/N, similarly to the method

described in McGraw et al. (2022), we define a cut-off S/N of ~ 30 . Of these eight observations, only 18 May 2019, one of the observations with a potential band (defined as having a band depth greater than the 1σ error but less than the 2σ error) has a low S/N-spectrum. Band depths at $2.9\ \mu\text{m}$ vary from $-0.5 \pm 3.3\%$ (25 March 2019) to $7.9 \pm 7.4\%$ (18 May 2019); including only high S/N observations, the maximum band depth detected is $2.8 \pm 1.4\%$ (13 December 2018).

Of the seven Rivkin et al. (2018) observations (one night was split into two datasets, making eight total spectra; see tables 1 & 2 in Rivkin et al. 2018 for observing parameters) that were run through our thermal model (Figure 3.4), three have a definite feature (i.e., band depth $>2\sigma$), two have a potential feature, and the remaining three do not have a feature. Again setting the S/N cut-off to ~ 30 and qualitatively assessing the longer wavelength spectral shape for unexpected reflectance variations, the observation made on 6 December 2011 is the only observation with a low S/N spectrum. The band depths range from $0.5 \pm 1.4\%$ (27 August 2011) to $8.7 \pm 6.3\%$ (6 December 2011); including only high S/N observations the maximum band depth detected is $5.0 \pm 1.8\%$ (4 June 2012). Combining both datasets, the $2.9\ \mu\text{m}$ band depth ranges from $-0.5 \pm 3.3\%$ (25 March 2019) to $8.7 \pm 6.3\%$ (6 December 2011) for all observations and from $-0.5 \pm 3.3\%$ (25 March 2019) to $5.0 \pm 1.8\%$ (4 June 2012) when only considering the observations with high S/N spectra. The band depths at each of the five measured wavelengths for each observation are reported in Table 3.4.

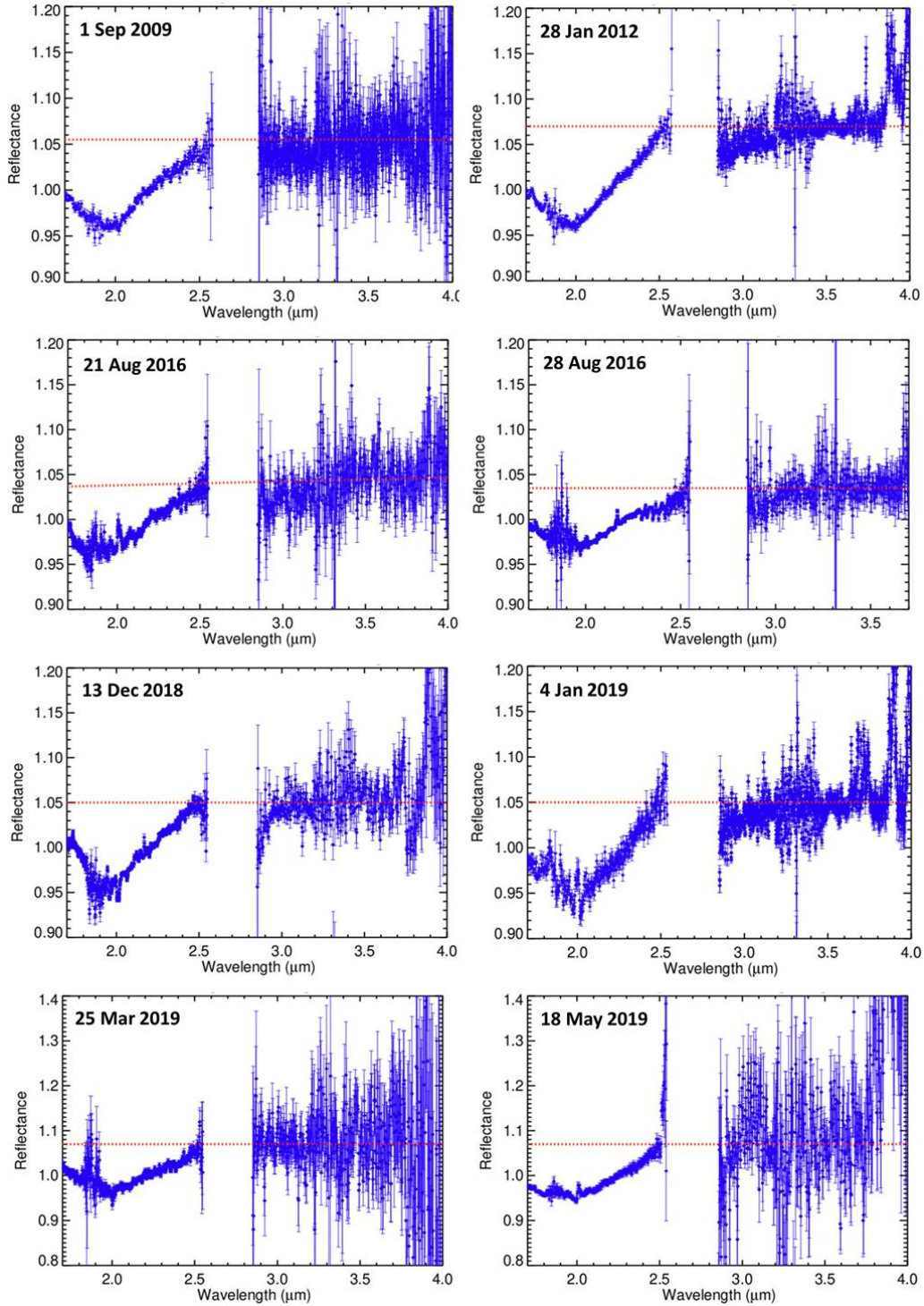


Figure 3.2: LXD spectra of Eros collected during McGraw et al. (2022) campaign. Blue points are reflected data after thermal tail removal and red dashed line is the best-fit reflected continuum. All spectra binned by a factor of 9. The prism spectrum is plotted instead of LXD at shorter wavelengths for 1 Sep 2009, 28 Jan 2012, 4 Jan 2019, and 18 May 2019 observations due to noise.

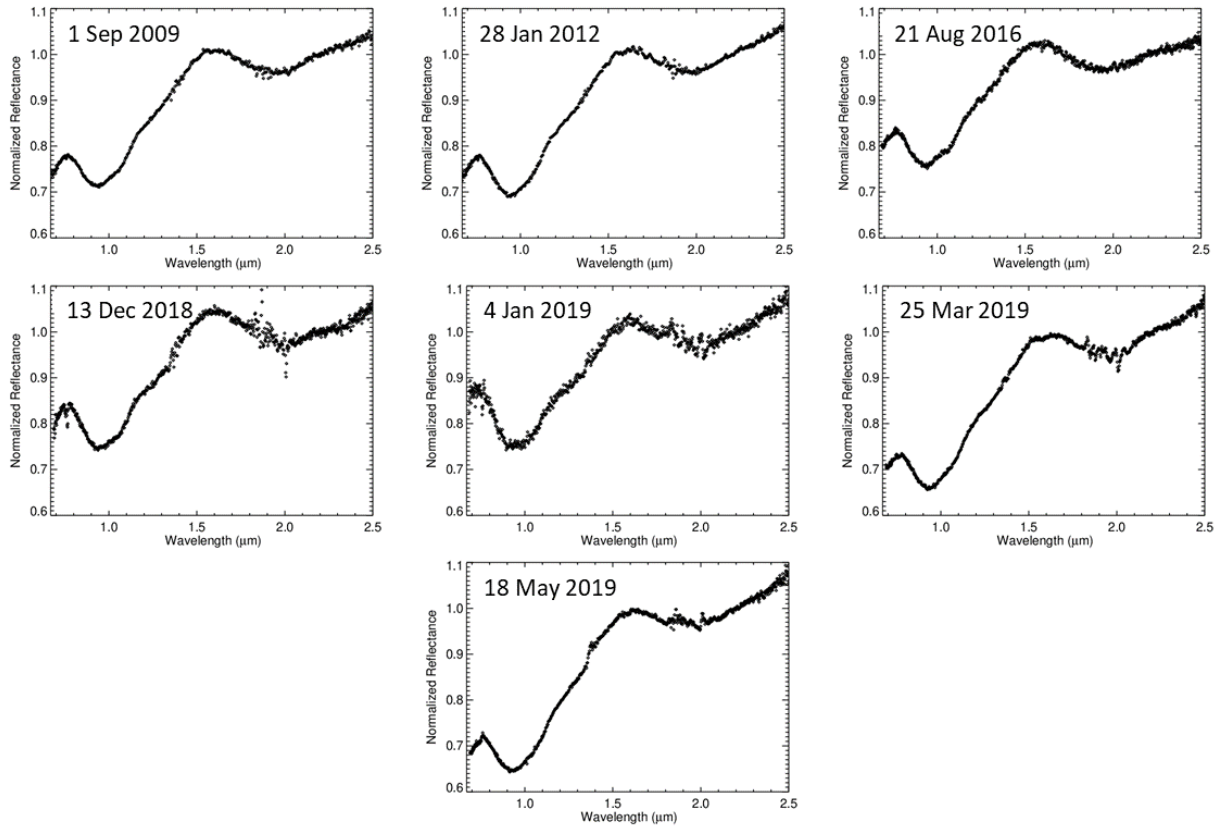


Figure 3.3: Prism spectra of Eros collected during McGraw et al. (2022) campaign.

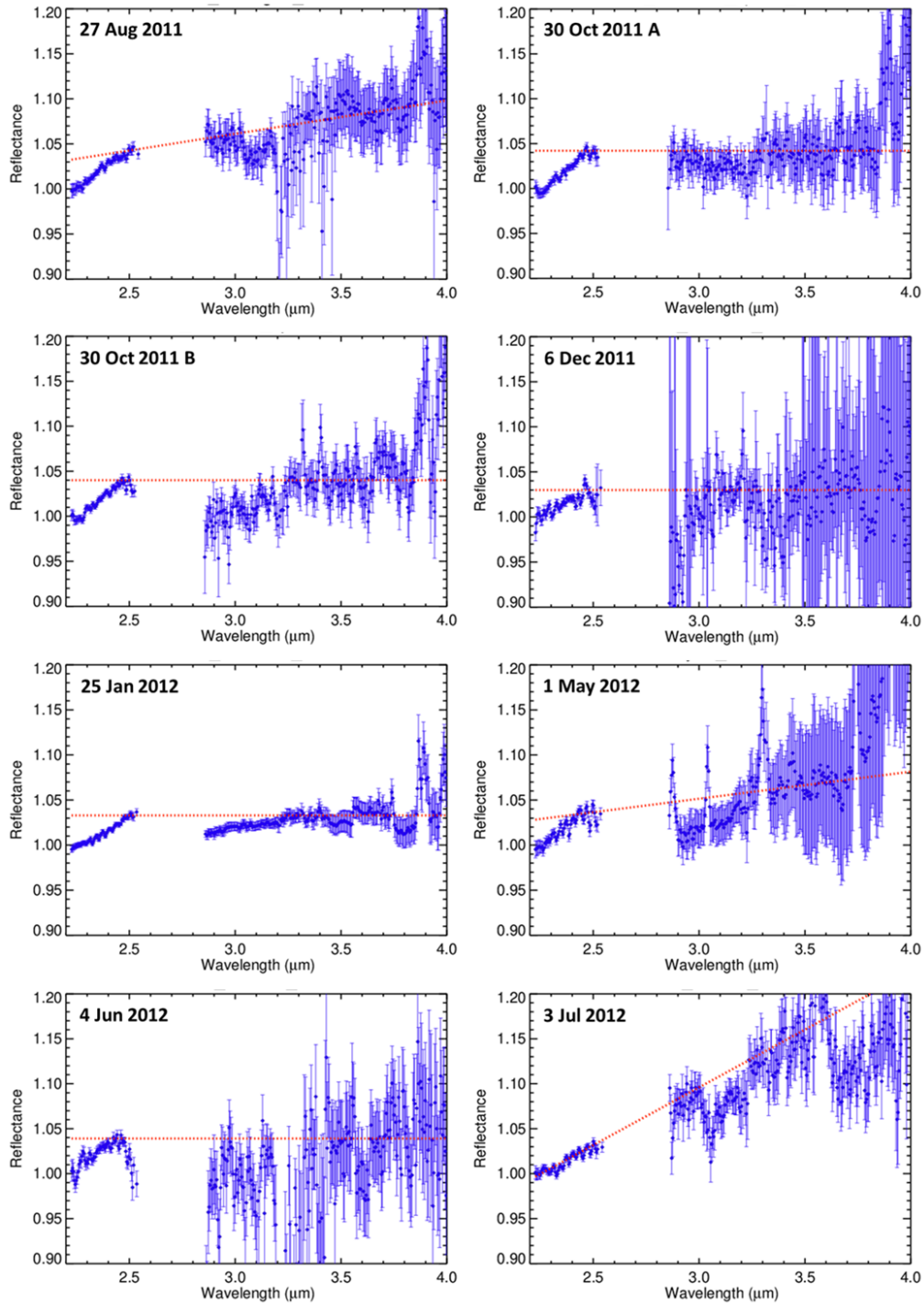


Figure 3.4: Remodeled LXD spectra of Eros collected during Rivkin et al. (2018) campaign. Blue points are reflected data after thermal tail removal and red dashed line is the best-fit reflected continuum. All spectra binned by a factor of 9.

Table 3.4: Band depths with 1σ errors for (433) Eros

Date (UT)	2.9- μ m band?	2.9- μ m Band Depth	2.95- μ m Band Depth	3.0- μ m Band Depth	3.05- μ m Band Depth	3.1- μ m Band Depth
McGraw et al. Observations						
1-Sep-2009	No	$1.5 \pm 2.1\%$	$1.2 \pm 2.0\%$	$1.7 \pm 1.9\%$	$1.1 \pm 2.2\%$	$1.6 \pm 2.1\%$
28-Jan-2012	Yes	$2.7 \pm 1.3\%$	$2.7 \pm 1.1\%$	$2.0 \pm 1.2\%$	$1.4 \pm 1.2\%$	$1.5 \pm 1.2\%$
21-Aug-2016	Maybe	$2.7 \pm 1.8\%$	$2.1 \pm 2.1\%$	$1.2 \pm 1.9\%$	$2.2 \pm 2.5\%$	$2.0 \pm 1.8\%$
28-Aug-2016	Maybe	$2.3 \pm 1.6\%$	$2.2 \pm 1.6\%$	$1.4 \pm 1.7\%$	$0.4 \pm 1.6\%$	$0.3 \pm 1.7\%$
13-Dec-2018	Yes	$2.8 \pm 1.4\%$	$0.7 \pm 1.1\%$	$0.8 \pm 0.9\%$	$0.0 \pm 1.5\%$	$0.3 \pm 1.3\%$
4-Jan-2019	Maybe	$2.4 \pm 1.5\%$	$2.2 \pm 1.3\%$	$1.6 \pm 1.4\%$	$1.4 \pm 1.3\%$	$1.5 \pm 1.3\%$
25-Mar-2019	No	$-0.5 \pm 3.3\%$	$-0.9 \pm 2.1\%$	$-0.1 \pm 2.7\%$	$0.0 \pm 2.0\%$	$-0.1 \pm 2.1\%$
<i>18-May-2019</i>	<i>Maybe</i>	<i>$7.9 \pm 7.4\%$</i>	<i>$2.5 \pm 3.3\%$</i>	<i>$-4.6 \pm 5.8\%$</i>	<i>$-6.2 \pm 6.1\%$</i>	<i>$-4.3 \pm 7.3\%$</i>
Rivkin et al. Observations						
27-Aug-2011	No	$0.5 \pm 1.4\%$	$0.6 \pm 1.5\%$	$0.6 \pm 1.7\%$	$2.1 \pm 1.6\%$	$2.8 \pm 1.4\%$
30-Oct-2011 A	No	$1.2 \pm 1.4\%$	$0.6 \pm 1.5\%$	$0.8 \pm 1.4\%$	$1.9 \pm 1.4\%$	$1.8 \pm 1.3\%$
30-Oct-2011 B	Yes	$4.0 \pm 1.7\%$	$3.8 \pm 1.4\%$	$2.9 \pm 1.4\%$	$3.9 \pm 1.3\%$	2.5 ± 1.6
<i>6-Dec-2011</i>	<i>Maybe</i>	<i>$8.7 \pm 6.3\%$</i>	<i>$2.6 \pm 23.9\%$</i>	<i>$2.7 \pm 2.1\%$</i>	<i>$1.7 \pm 3.3\%$</i>	<i>$-0.1 \pm 1.7\%$</i>
25-Jan-2012	Yes	$1.8 \pm 0.8\%$	$1.5 \pm 0.9\%$	$1.2 \pm 0.8\%$	$1.1 \pm 0.8\%$	$1.1 \pm 0.7\%$
1-May-2012	Maybe	$2.8 \pm 1.9\%$	$3.6 \pm 1.0\%$	$3.1 \pm 0.8\%$	$1.1 \pm 2.5\%$	$3.0 \pm 0.7\%$
4-Jun-2012	Yes	$5.0 \pm 1.8\%$	$2.4 \pm 2.5\%$	$3.6 \pm 2.8\%$	$4.2 \pm 2.6\%$	$5.5 \pm 2.6\%$
3-Jul-2012	No	$0.7 \pm 1.5\%$	$0.9 \pm 1.7\%$	$0.9 \pm 1.6\%$	$4.8 \pm 1.6\%$	$3.8 \pm 1.3\%$

Rows in italics signify low S/N observations

3.3.2 (1036) Ganymed

We made six observations of Ganymed (Tables 3.2 & 3.3 and Figure 3.5), two of which (10 June 2011 and 4 July 2011) were previously published by Wigton (2015) and Rivkin et al. (2018) and were re-extracted to ensure equal comparison with subsequently collected data. The 4 July 2011 spectrum had residual atmospheric contamination after processing and thermal modelling, so a manual atmospheric correction was applied to divide out the remainder. We obtained prism spectra for all six observations (Figure 3.6). We also re-processed 28 August

2011 from Rivkin et al. (2018) to verify that the differing extracting and processing methods described in Section 3.3.1 do not yield significantly different band depths.

Of the seven datasets we processed from the raw data, one exhibits a definite band, four exhibit a potential band, and two do not have a band. The observations from 31 October 2020 and 9 December 2020, which have a potential band and no band, respectively, have low S/N spectra using the same cutoff as used for Eros (Section 3.3.1). Band depths at $2.9\ \mu\text{m}$ vary from $0.8 \pm 1.1\%$ (26 September 2011) to $3.7 \pm 2.2\%$ (31 October 2020). The deepest band of the high-S/N spectra is from the 10 June 2011 observation ($2.9 \pm 1.5\%$).

Of the six re-modelled Rivkin et al. (2018) observations (Figure 3.7; see tables 1 & 3 in Rivkin et al. 2018 for observing parameters), two have a potential feature and the remaining four do not have a feature. The observation made on 6 December 2011 has a low S/N spectrum, though the S/N at longer wavelengths within the band is higher. The band depths range from $0.6 \pm 1.5\%$ (5 July 2011) to $1.9 \pm 1.4\%$ (30 October 2011). The $2.9\text{-}\mu\text{m}$ band depth range of the re-modelled Rivkin data encompasses the band depth range of the previously described dataset. The band depths at each of the five measured wavelengths for each observation are reported in Table 3.5.

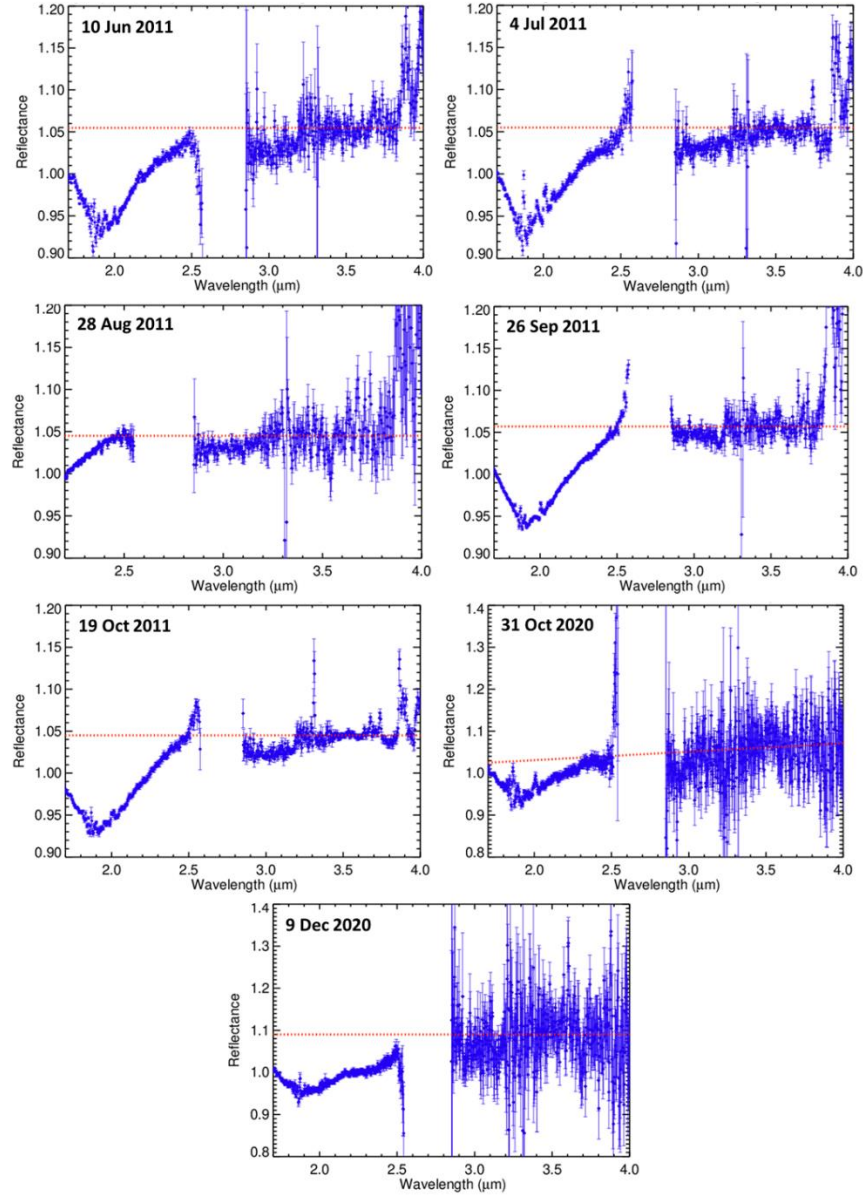


Figure 3.5: LXD spectra of Ganymed collected during McGraw et al. (2022) campaign (28 Aug 2011 data from Rivkin et al. (2018) campaign). Blue points are reflected data after thermal tail removal and red dashed line is the best-fit reflected continuum. All spectra binned by a factor of 9. The prism spectrum is plotted instead of LXD at shorter wavelengths for all observations except 28 Aug 2011 due to noise.

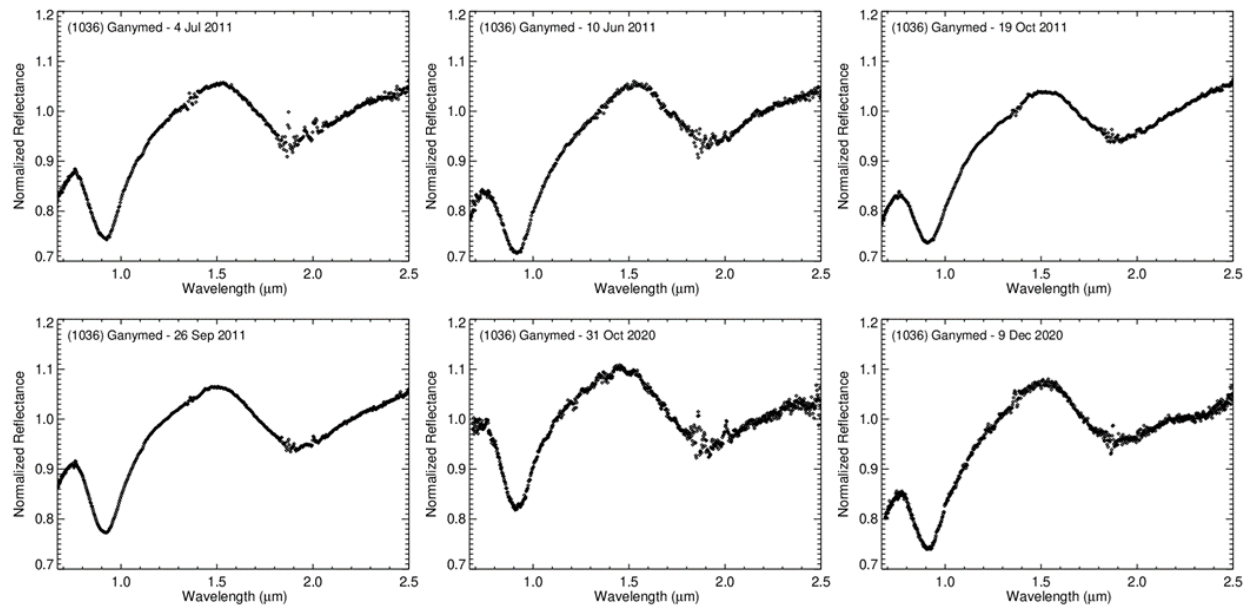


Figure 3.6: Prism spectra of Ganymed collected during McGraw et al. (2022) campaign.

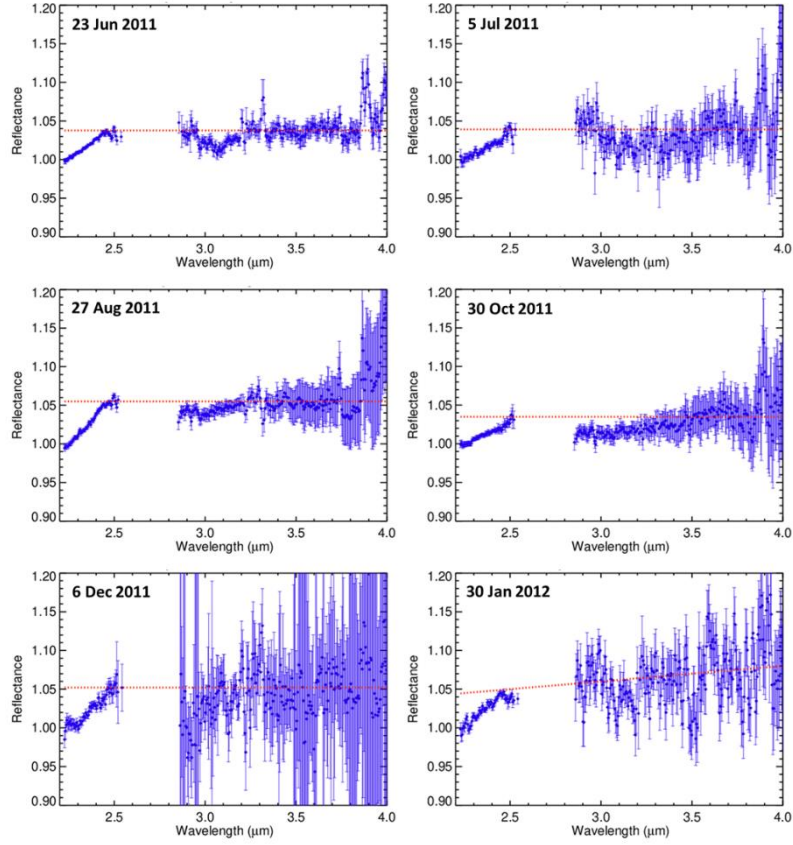


Figure 3.7: Remodeled LXD spectra of Ganymed collected during Rivkin et al. (2018) campaign. Blue points are reflected data after thermal tail removal and red dashed line is the best-fit reflected continuum. All spectra binned by a factor of 9.

Table 3.5: Band depths with 1σ errors for (1036) Ganymed

Date (UT)	2.9- μ m band?	2.9- μ m Band Depth	2.95- μ m Band Depth	3.0- μ m Band Depth	3.05- μ m Band Depth	3.1- μ m Band Depth
McGraw et al. Observations						
10-Jun-2011	Yes	$2.9 \pm 1.5\%$	$2.5 \pm 1.4\%$	$3.0 \pm 1.5\%$	$2.8 \pm 1.5\%$	$1.8 \pm 1.6\%$
4-Jul-2011	Maybe	$2.4 \pm 1.4\%$	$2.5 \pm 1.3\%$	$2.3 \pm 1.2\%$	$2.2 \pm 1.2\%$	$2.3 \pm 1.3\%$
28-Aug-2011	Maybe	$1.7 \pm 1.2\%$	$1.4 \pm 1.1\%$	$1.3 \pm 1.0\%$	$1.4 \pm 1.0\%$	$1.5 \pm 1.2\%$
26-Sep-2011	No	$0.8 \pm 1.1\%$	$1.2 \pm 1.1\%$	$0.8 \pm 1.0\%$	$0.9 \pm 1.0\%$	$1.1 \pm 1.0\%$
19-Oct-2011	Maybe	$1.7 \pm 1.3\%$	$2.2 \pm 1.2\%$	$2.3 \pm 1.2\%$	$2.0 \pm 1.2\%$	$1.8 \pm 1.2\%$
<i>31-Oct-2020</i>	<i>Maybe</i>	<i>$3.7 \pm 2.2\%$</i>	<i>$5.5 \pm 2.7\%$</i>	<i>$1.9 \pm 3.3\%$</i>	<i>$2.2 \pm 4.8\%$</i>	<i>$1.2 \pm 5.0\%$</i>
<i>9-Dec-2020</i>	<i>No</i>	<i>$1.1 \pm 2.8\%$</i>	<i>$4.6 \pm 3.3\%$</i>	<i>$3.1 \pm 3.1\%$</i>	<i>$2.7 \pm 4.3\%$</i>	<i>$1.2 \pm 4.9\%$</i>
Rivkin et al. Observations						
23-Jun-2011	No	$0.6 \pm 1.3\%$	$0.6 \pm 1.6\%$	$1.4 \pm 1.2\%$	$2.1 \pm 1.3\%$	$2.0 \pm 1.2\%$
5-Jul-2011	No	$-0.6 \pm 1.5\%$	$-1.2 \pm 1.7\%$	$1.1 \pm 1.8\%$	$1.3 \pm 1.3\%$	$3.0 \pm 1.4\%$
27-Aug-2011	Maybe	$1.1 \pm 0.9\%$	$1.1 \pm 0.9\%$	$1.6 \pm 0.8\%$	$1.1 \pm 0.8\%$	$0.8 \pm 0.8\%$
30-Oct-2011	Maybe	$1.9 \pm 1.4\%$	$2.2 \pm 1.6\%$	$2.1 \pm 1.4\%$	$2.3 \pm 1.5\%$	$1.7 \pm 1.5\%$
<i>6-Dec-2011</i>	<i>No</i>	<i>$5.5 \pm 7.1\%$</i>	<i>$4.6 \pm 18.8\%$</i>	<i>$1.6 \pm 2.0\%$</i>	<i>$2.3 \pm 2.9\%$</i>	<i>$-0.5 \pm 1.7\%$</i>
30-Jan-2012	No	$0.1 \pm 2.9\%$	$-1.2 \pm 2.3\%$	$-1.7 \pm 2.8\%$	$1.5 \pm 2.6\%$	$3.1 \pm 2.6\%$

Rows in italics signify low S/N observations

3.3.3 (3122) Florence

We made two observations of Florence (Tables 3.2 & 3.3 and Figure 3.8), one of which (5 August 2010) was previously published by Wigton (2015) and was re-extracted to ensure equal comparison with subsequently collected data. The second observation was made on 4 September 2017, and the global average spectrum was published in McGraw et al. (2022). Here, we analyze an average spectrum that was run through a more refined thermal model than was used by McGraw et al. (2022), though the band depths and errors are nearly identical. We also separate the observing run into four spectra to assess any rotational variability in the band (Figure 3.9), as described in Section 3.2.1. Prism data were collected for the 4 September 2017 observation but not for the 5 August 2010 observation.

All five spectra of Florence from 4 September 2017 (the global average and four rotationally resolved spectra) have very high S/N, with only one below 100. However, the spectrum from 5 August 2010 only has a S/N of 9 and has an irregular spectral shape at longer wavelengths, so it is considered a low S/N spectrum. Given the almost sinusoidal spectral shape from 2.85 μm to 4.0 μm in the 2010 data, the apparent feature from 2.9 μm to 3.1 μm cannot be trusted and thus this spectrum will not be included in the ensuing discussion of band depth and shape variations on Florence. The average spectrum and spectrum of the second set of frames (midtime 08:30 UTC) have potential bands at 2.9 μm ; the other spectra do not exhibit a band at that wavelength. The average band depth at 2.9 μm for the 4 September 2017 observation is $1.9 \pm 1.8\%$ and the band depths range from $1.4 \pm 1.6\%$ to $2.3 \pm 1.2\%$ for the rotationally resolved spectra. We also binned the spectra by another factor of 4.5 in order to simplify and further study the subtle differences in band shape at different longitudes. The band depths of these further binned spectra are nearly the same as those reported, as expected. Band depths for both observations at all measured wavelengths and rotational positions are reported in Table 3.6.

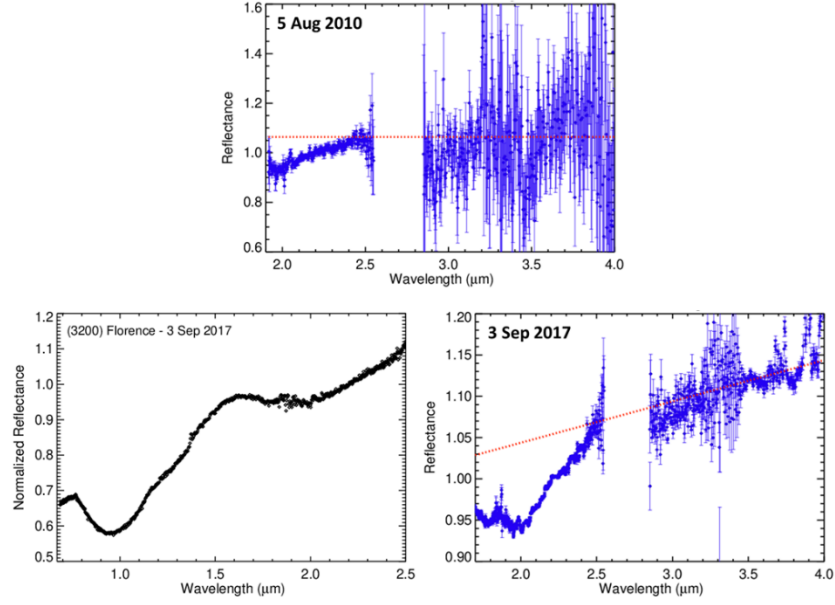


Figure 3.8: Spectra of Florence collected during Wigton (2015) and McGraw et al. (2022) campaigns. For LXD, blue points are reflected data after thermal tail removal and red dashed line is the best-fit reflected continuum. LXD spectra binned by a factor of 9.

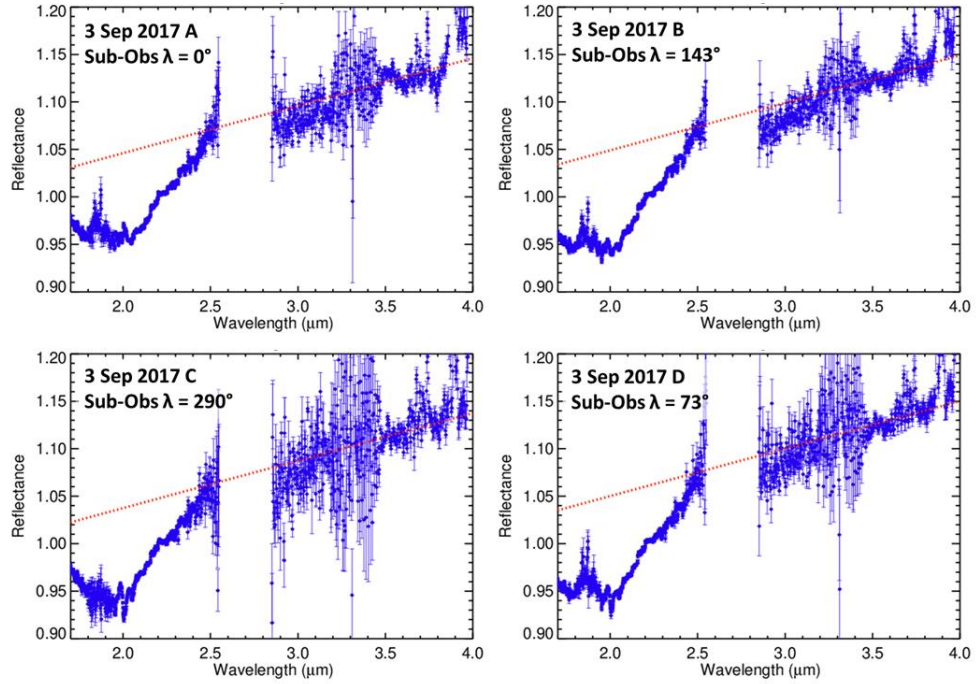


Figure 3.9: Rotationally resolved spectra of Florence collected on 3 Sep 2017 during McGraw et al. (2022) campaign. Blue points are reflected data after thermal tail removal and red dashed line is the best-fit reflected continuum. All spectra binned by a factor of 9.

Table 3.6: Band depths with 1σ errors for (3122) Florence

Date (UT)	2.9- μm band?	2.9- μm Band Depth	2.95- μm Band Depth	3.0- μm Band Depth	3.05- μm Band Depth	3.1- μm Band Depth
<i>5-Aug-2010</i>	<i>Maybe</i>	$13.0 \pm 9.0\%$	$12.4 \pm 8.4\%$	$6.5 \pm 6.4\%$	$6.7 \pm 6.5\%$	$7.7 \pm 5.6\%$
3-Sep-2017 Avg	Maybe	$1.9 \pm 1.8\%$	$1.8 \pm 1.4\%$	$1.4 \pm 1.2\%$	$1.0 \pm 1.3\%$	$0.9 \pm 1.7\%$
3-Sep-2017 A	No	$1.4 \pm 1.6\%$	$1.7 \pm 1.2\%$	$1.2 \pm 1.2\%$	$1.2 \pm 1.1\%$	$1.2 \pm 1.4\%$
3-Sep-2017 B	Maybe	$2.3 \pm 1.2\%$	$2.2 \pm 1.0\%$	$1.7 \pm 0.8\%$	$1.2 \pm 1.0\%$	$1.1 \pm 1.1\%$
3-Sep-2017 C	No	$2.1 \pm 2.8\%$	$1.5 \pm 1.9\%$	$1.2 \pm 1.6\%$	$1.1 \pm 1.7\%$	$0.2 \pm 2.4\%$
3-Sep-2017 D	No	$1.5 \pm 2.0\%$	$1.6 \pm 1.6\%$	$1.1 \pm 1.5\%$	$0.8 \pm 1.4\%$	$0.5 \pm 1.8\%$

Rows in italics signify low S/N observations

3.4 Analysis

3.4.1 Band Parameter Analysis

3.4.1.1 Prism Bands

Band parameters and mineralogical determinations with all necessary corrections, as described in Section 3.2.3.1, are reported in Table 3.7 for all Eros, Ganymed, and Florence observations for which prism data were collected. Additionally, BIC and BAR are plotted in Figure 3.10, along with

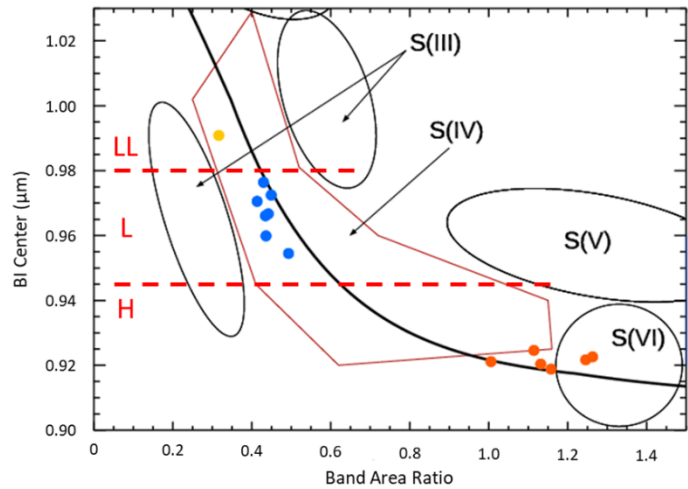


Figure 3.10: Zoomed in Gaffey et al. (1993) S-subtypes plot with ordinary chondrite division lines from Dunn et al. (2010). (433) Eros is plotted in blue, (1036) Ganymed is plotted in orange, and (3122) Florence is plotted in yellow.

different S-complex asteroid sub-types defined by Gaffey et al. (1993) and ordinary chondrite types defined by Dunn et al. (2010). The BAR values in Table 3.7 and on Figure 3.10 are temperature- and red edge-corrected. The Sanchez et al. (2020) equations for olivine ratio include their own red edge correction, so the version of the BARs we input into that equation is only temperature-corrected. . All observations of Eros and Florence plot in the S(IV) region, the

only region for which the Sanchez et al. (2020) equations are intended. Florence plots in the LL ordinary chondrite region and Eros plots in the L ordinary chondrite region, according to Dunn et al. (2010).

Ganymed plots outside this region, with two points in the S(VI) region and the remaining four in the space between the S(IV) and S(VI) regions, even though it is an S-complex asteroid (specifically, Sr-type). However, plots of fayalite mole percent (Fa) and ferrosillite mole percent (Fs) vs. olivine to total olivine and pyroxene ratio ($ol/(ol+px)$) from Dunn et al. (2010) and an Fs vs. Fa plot from Lucas et al. (2018) show that all observations of Ganymed match the higher-iron content H ordinary chondrites (Figure 3.11). These plots, which delineate the three ordinary chondrite groups more robustly than on the Gaffey S subtypes plot (Dunn et al. 2010), also show Eros as more closely aligning with LL ordinary chondrites, rather than L chondrites as seen on the Gaffey plot (Figure 3.10). Florence still plots as an LL chondrite.

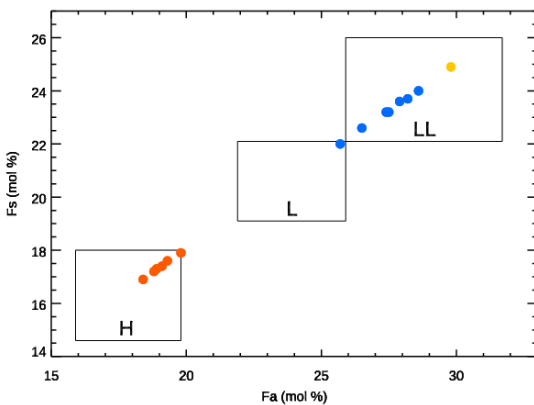


Figure 3.11: Modified ferrosilite vs. fayalite plot from Lucas et al. (2018) showing ordinary chondrite sub-types. (433) Eros is plotted in blue, (1036) Ganymed is plotted in orange, and (3122) Florence is plotted in yellow.

Table 3.1: Band Parameters for Eros, Ganymed, and Florence

Date (UT)	Fa	Fs	ol/ol+pyx	BIC	BIIC*	BAR**
(433) Eros						
1-Sep-2009	27.9 ± 0.4	23.6 ± 0.2	0.630 ± 0.001	0.971 ± 0.003	1.981 ± 0.004	0.413 ± 0.005
28-Jan-2012	27.5 ± 0.3	23.2 ± 0.2	0.623 ± 0.001	0.967 ± 0.002	2.005 ± 0.004	0.442 ± 0.004
21-Aug-2016	25.7 ± 0.2	22.0 ± 0.1	0.611 ± 0.001	0.954 ± 0.001	1.950 ± 0.003	0.493 ± 0.004
13-Dec-2018	28.6 ± 0.4	24.0 ± 0.3	0.626 ± 0.001	0.976 ± 0.004	2.011 ± 0.002	0.430 ± 0.006
4-Jan-2019	28.2 ± 1.5	23.7 ± 1.1	0.621 ± 0.002	0.972 ± 0.013	2.011 ± 0.006	0.449 ± 0.009
25-Mar-2019	26.5 ± 0.3	22.6 ± 0.3	0.624 ± 0.002	0.960 ± 0.002	2.016 ± 0.001	0.436 ± 0.007
18-May-2019	27.4 ± 0.4	23.2 ± 0.3	0.625 ± 0.002	0.966 ± 0.003	2.013 ± 0.005	0.434 ± 0.007
(1036) Ganymed						
10-Jun-2011	18.9 ± 0.2	17.3 ± 0.2	0.499 ± 0.001	0.921 ± 0.001	1.930 ± 0.002	1.006 ± 0.006
4-Jul-2011	19.8 ± 0.2	17.9 ± 0.2	0.472 ± 0.003	0.925 ± 0.001	1.896 ± 0.001	1.114 ± 0.014
26-Sep-2011	19.3 ± 0.2	17.6 ± 0.2	0.438 ± 0.002	0.923 ± 0.001	1.924 ± 0.001	1.263 ± 0.007
19-Oct-2011	19.1 ± 0.2	17.4 ± 0.2	0.442 ± 0.004	0.922 ± 0.001	1.926 ± 0.002	1.246 ± 0.015
31-Oct-2020	18.4 ± 0.5	16.9 ± 0.4	0.462 ± 0.009	0.919 ± 0.002	1.920 ± 0.002	1.158 ± 0.036
9-Dec-2020	18.8 ± 0.2	17.2 ± 0.2	0.469 ± 0.004	0.920 ± 0.001	1.902 ± 0.003	1.132 ± 0.016
(3122) Florence						
3-Sep-2017	29.8 ± 0.3	24.9 ± 0.2	0.652 ± 0.001	0.991 ± 0.004	2.016 ± 0.002	0.317 ± 0.004

*Temperature-corrected

**Temperature- & red-edge-corrected

3.4.1.2 OH/H₂O Band

Numerous studies have classified 3- μ m bands on asteroids to determine volatile composition and delivery mechanisms (e.g., Rivkin 2010; Takir & Emery 2012; Rivkin et al. 2019), though only McGraw et al. (2022) focused on NEAs. The four band shape classifications discussed in McGraw et al. (2022) can be further simplified into two general groups, linear and rounded, where the linear bands generally indicate OH and the rounded bands generally indicate the presence of H₂O, possibly in addition to OH (e.g., Takir & Emery 2012). As described in McGraw et al. (2022), Eros exhibited a linear band while Ganymed and Florence exhibited

rounded, or bowl-like, bands. While the spectra reported herein exhibit some variations, the bands present in these observations generally still fit into those same categories.

3.4.1.2.1 (433) Eros

The eleven Eros spectra with (potential) features primarily exhibit sharp, linear features, with some variation in band width. These bands closely resemble the “sharp” and “Pallas-type” shapes described in Takir & Emery (2012) and Rivkin et al. (2019), respectively, as well as the “wide linear” (type 1) and “narrow linear” (type 2) shapes described in McGraw et al. (2022). This band shape is typically attributed to hydroxide in phyllosilicates or unbound molecules (e.g., Lebofsky 1980). These bands are linear features that sharply increase from $\sim 2.85 \mu\text{m}$ to the reflected continuum between 3.0 and $3.25 \mu\text{m}$.

Three of the eleven spectra with (potential) bands do not fall into the “linear” category: 28 January 2012, 1 May 2012, and 4 June 2012. The latter has a large point-to-point spread in the 2-4- μm region, so its shape cannot be classified. The features present on the January and May observations are rounded (or bowl-like), shallow, and slightly curved from ~ 2.85 to $\sim 3.15 \mu\text{m}$ before curving more sharply to intersect the continuum at $\sim 3.2 \mu\text{m}$. These two bands are most similar to the wide bowl (type 3) band shape described in McGraw et al. (2022) and the rounded group in Takir & Emery’s (2012), who attributed it to water ice on large Main Belt asteroids. Ammonia-bearing species are also theorized to cause a bowl-like spectral shape, as seen by Dawn and Rosetta observations of Ceres (De Sanctis et al. 2018) and 67P (Poch et al. 2020), respectively.

3.4.1.2.2 (1036) Ganymed

All seven of the Ganymed spectra with (potential) features at $2.9 \mu\text{m}$ exhibit rounded, bowl-like features. These features vary in width, though most of them are nearly identical to the

wide bowl (type 3) shape described in McGraw et al. (2022), which was typified by Ganymed in that study. Two spectra with no 2.9- μm absorption feature, 23 June 2011 and 30 January 2012, have potential features (i.e., to 1σ) at longer wavelengths. Both features are also generally bowl-like, with the band as observed on 23 June 2011 extending from ~ 2.96 to ~ 3.2 μm and the band from 30 January 2012 extending from ~ 3.1 to ~ 3.2 μm .

3.4.1.2.3 (3122) Florence

The average spectrum of Florence exhibits a shape most closely related to the narrow bowl (type 4) shape described in McGraw et al. (2022), though the narrow bowl appears to be superimposed on a wider feature when binned to a higher degree. We arbitrarily set the first group of frames as our sub-observer 0° longitude (Table 3.3). This spectrum (Figure 3.12a) exhibits a wide bowl-like shape, similar to the type 3 in the McGraw et al. (2022) study, and has the shallowest band depth of the Florence spectra at 2.9 μm (Table 3.6). Florence rotated approximately 145° between the midtime of each set of frames and given that Florence is roughly spheroidal with a spin pole $\approx 90^\circ$ (Franco et al. 2018), the second set of Florence frames has a midtime relative longitude of $\sim 145^\circ$ ($\text{lon} = 142.5^\circ$). This spectrum has the highest S/N of the Florence dataset and exhibits a band shape nearly identical to that of the average (Figure 3.12b). The band depth at all measured wavelengths is deepest for this spectrum (Table 3.6). The third set of frames has a midtime relative longitude of $\sim 290^\circ$ ($\text{lon} = 290.1^\circ$) and exhibits a wide linear band shape (Figure 3.12c), similar to what is seen on Eros. This spectrum has the lowest S/N and its band is too shallow to even be identified as a potential band; it is the only Florence spectrum to have no band at all measured wavelengths. The final set of frames has a midtime relative longitude of $\sim 75^\circ$ ($\text{lon} = 72.6^\circ$), after subtracting 360° , and has a narrow bowl-

like shape, similar to the feature seen at $\text{lon} = 0^\circ$, though it is not superimposed on a larger feature (Figure 3.12d).

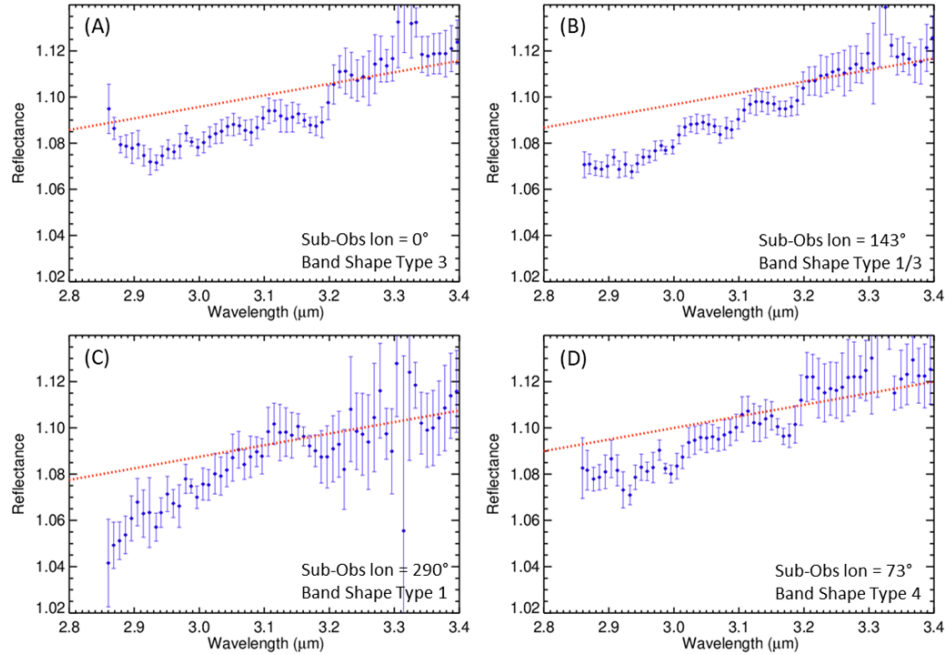


Figure 3.12: Rotationally resolved spectra of Florence collected on 3 Sep 2017 during McGraw et al. (2022) campaign, zoomed to highlight OH/H₂O absorption feature. Blue points are reflected data after thermal tail removal and red dashed line is the best-fit reflected continuum. All spectra binned by a factor of ~ 40 .

3.4.2 Characteristics Comparisons

We compared numerous observational, physical, and orbital characteristics to search for trends explaining the variation in band depths reported for Eros and Ganymed. Any variability in Florence’s band depth and shape in this study is attributed to surface features, since Florence did not move substantially in its orbit during the observation and as all spectra were collected during a single night. We compared object visible magnitude, heliocentric and observer distance, surface location (sub-observer and sub-solar), days since perihelion, phase angle, surface temperature (equilibrium and sub-solar), near-infrared (0.84-2.4 μm) slope, and surface mineralogy (band parameters) against band depth for each asteroid and at each wavelength

studied. We investigated potential trends in local solar time as well, though only for Ganymed, as Eros' polar orientation should prevent diurnal variations. We also looked at all those properties against various reflectance ratios, which were used as band shape proxies in Rivkin et al. (2018). We also considered the selected local standard star characteristics (i.e., visible magnitude and colors) in our analysis.

When considering the high S/N spectra, Eros exhibits potential trends between the 3.1-to-2.9 μm reflectance ratio and sub-observer latitude, band I center (and therefore fayalite and ferrosilite content), Earth distance, target V magnitude, and the ratio between local standard star V magnitude and that of Eros (Figures 3.13 & 3.14). The above trends also exist for the 3.1-to-2.95 μm reflectance ratio, but are weaker.

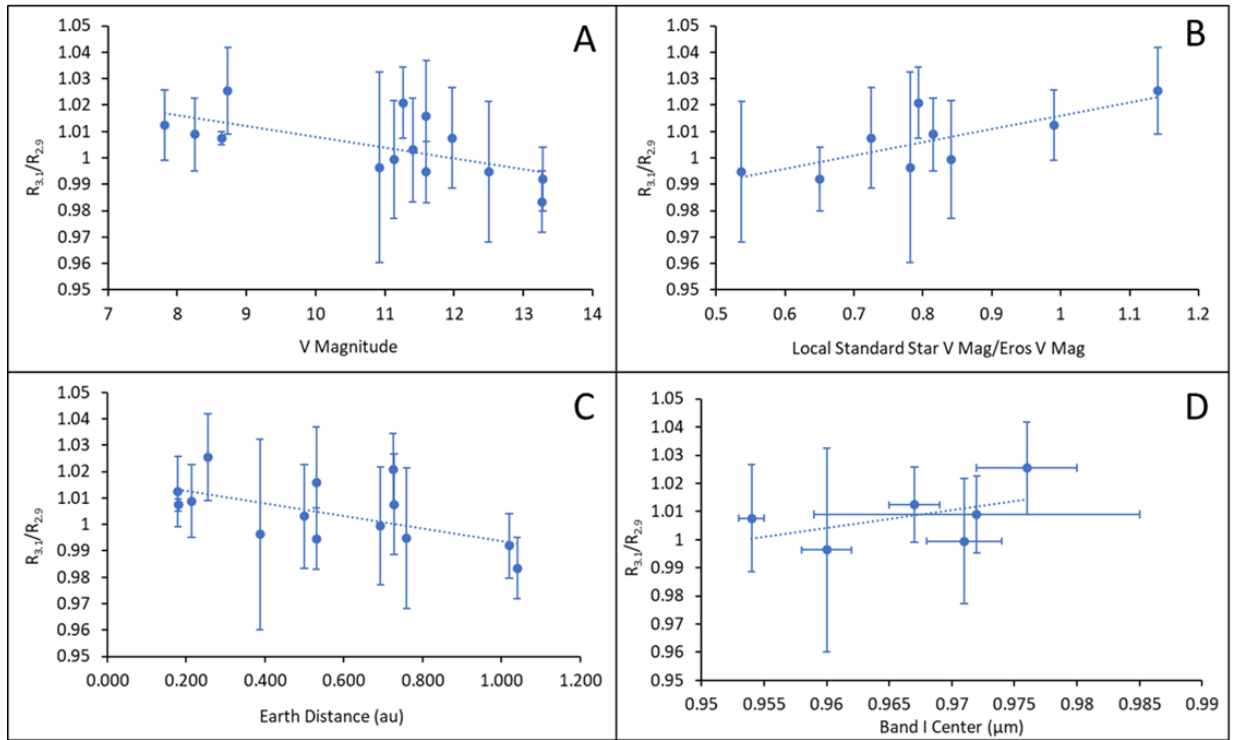


Figure 3.13: Plots for Eros showing the high S/N 3.1-to-2.9 μm reflectance ratio vs. Eros V magnitude (A), ratio of local standard star V magnitude to Eros V magnitude (B), Earth distance (C), and band I center (D). Dotted lines represent the best-fit linear trend.

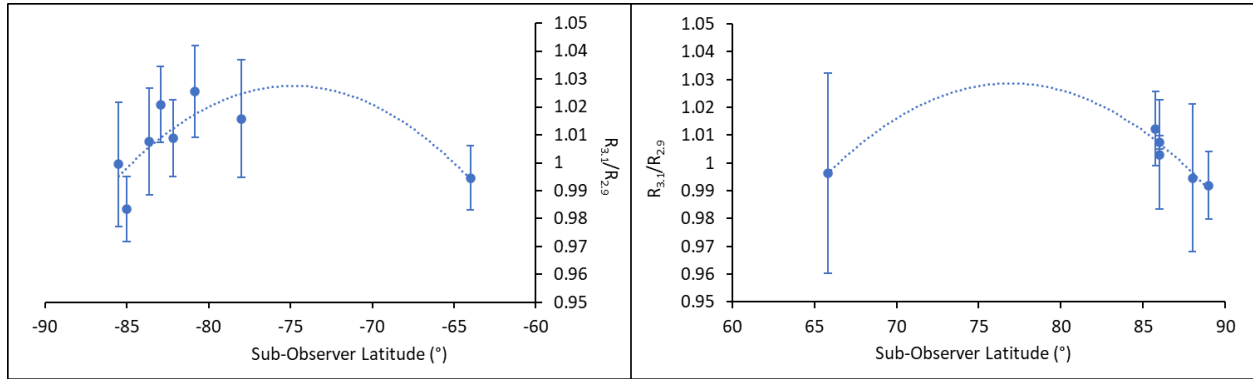


Figure 3.14: Plot for Eros showing the high S/N 3.1-to-2.9 μm reflectance ratio vs. sub-observer latitude. Dotted lines represent the best-fit parabolic trend.

Ganymed only exhibits potential trends between the band depth at 2.9 μm and sub-solar longitude (Figure 15) and between the band depth at all wavelengths and band I center. The latter trend is strongest when considering the band depth at 2.95 μm (Figure 3.16). There is significant overlap in error bars for all the above trends, so more observations are required to determine if these trends are real. Given that the observations of Eros and Ganymed were made over several years as well as under different weather conditions, the magnitude of band depth variations and the strength of the trends may be smaller/weaker or larger/stronger than reported, as observing circumstances affect the S/N and therefore the band depth/shape and associated error. However, effort was taken to ameliorate the consequences of this problem by comparing observational characteristics such as phase angle, Earth distance, and target visible magnitude against band depth and shape to separate observational and physical effects.

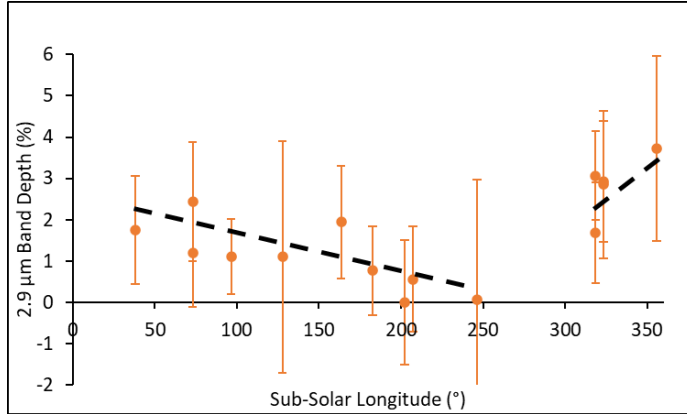
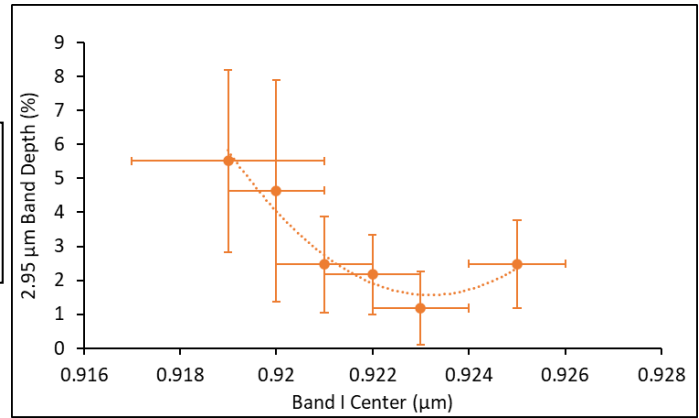


Figure 3.15: Plot for Ganymed showing the 2.9 μm band depth vs. sub-solar longitude. Dashed lines represent apparent best-fit trend.

Figure 3.16: Plot for Ganymed showing the 2.95 μm band depth vs. band I center. Dotted lines represent the best-fit parabolic trend.



3.5 Discussion

3.5.1 (433) Eros

Though some variation is present in the band shape exhibited by Eros, the average shape is best described as a sharp, shallow linear feature (see Section 3.4.1.2.1), which agrees with that seen by McGraw et al. (2022). We therefore also conclude that the volatile responsible for the 3-μm feature seen on Eros is OH that was delivered via solar wind hydrogen implantation. Spectral observations at wavelengths not visible from the ground are required to further test this hypothesis.

The potential trends with reflectance ratios, i.e., band shape, seen on Eros fall into two general categories: physical and observational. The first of the two physical trends, band shape versus sub-observer latitude, indicates a potential spatial dependence and uneven distribution of

OH across the surface, as the observed band is wider at the poles and narrows as latitude decreases. Given the lack of low-latitudinal 3- μm spectral coverage in both this dataset and in Rivkin et al. (2018), it is difficult to be certain about the latitudinal dependence and therefore to determine the cause of the spatial variability. However, provided the observed OH is delivered via solar wind hydrogen implantation, topographical variations could be responsible for preventing some areas from receiving hydrogen ions and helping other areas retain created OH. Eros' polar orientation could also explain this trend, as the poles point directly at the Sun for much of Eros' orbit (Taylor 1985), potentially enabling the build-up of OH. Alternatively, the other physical trend of band shape versus band I center suggests that the exact silicate composition may influence OH/H₂O delivery/retention, as the band is wider for higher iron content. The spatial dependence and compositional dependence may therefore be linked. A 10- and 20- μm spectral study would be useful in determining the importance of silicate composition on OH/H₂O delivery/retention, as the NIR can only be used to determine the olivine-pyroxene ratio and Mg/Fe content in olivines and pyroxenes. These mid-IR regions are the location of the bending and stretching modes, respectively, for several silicates including quartz, feldspars, pyroxenes, and amphiboles, and can also be used to determine the amorphous-crystalline ratio of the silicates present (e.g., Gupta 2003).

The remaining potential trends are observational in nature, and if real, might suggest the apparent variation in band depth on Eros is not linked to physical characteristics. These trends, band shape with Earth distance, target V magnitude, and standard star-to-Eros V magnitude ratio, are all coupled, as Eros would appear brighter closer to Earth. No trend was observed in standard star brightness, indicating the weak trend seen in its ratio with Eros' brightness is likely due only to the latter. Additionally, there is a slight correlation between Earth distance and sub-

observer latitude for the observations at latitudes higher than $\pm 80^\circ$ (Figure 3.17). Earth distance decreases as latitude decreases, indicating the potential trend in band shape with Earth distance might be due to physical effects rather than observational circumstances, as wider bands on Eros (i.e., higher R3.1/R2.9 values) are associated with both lower relative latitudes and Earth distances. Also, there is no correlation between S/N and band depth or shape, so the brightness of Eros does not affect the data quality. It is therefore more likely that the band depth and shape variations are due to some physical effect rather than observationally driven, even if no strong trends have yet been identified.

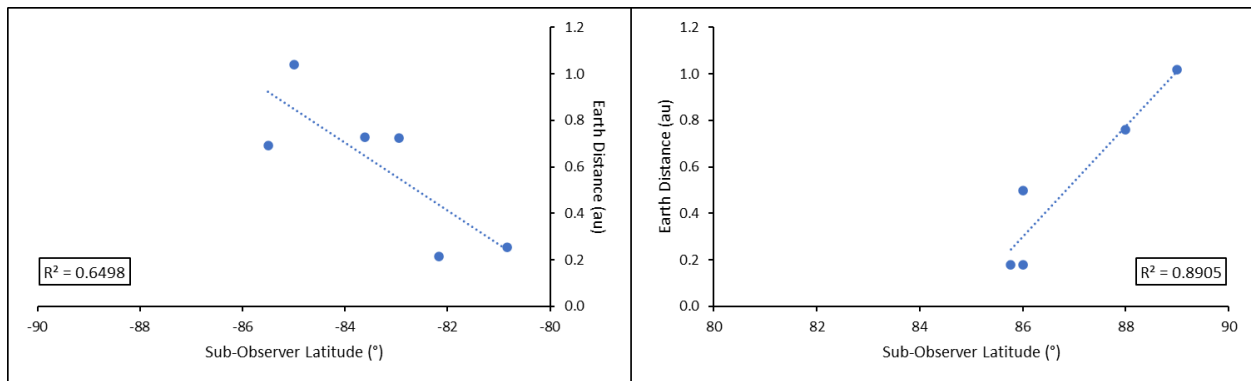


Figure 3.17: Plot for Eros showing Earth distance vs. sub-observer latitude. Dotted lines represent the best-fit linear trend, and the associated R^2 values are given.

3.5.2 (1036) Ganymed

The average shape seen on Ganymed is best described as a shallow bowl-like feature (see Section 3.4.1.2.2), which matches that seen by McGraw et al. (2022). As with Eros, we therefore also agree with their conclusion, that Ganymed's 3- μm feature indicates H_2O , or possibly even ammonia-bearing minerals, in addition to some OH is present and was delivered via carbonaceous and/or cometary impacts. The lack of a trend between band depth and local solar time further supports this hypothesis, as diurnal variations would be expected if Ganymed's OH/ H_2O was delivered via solar wind hydrogen implantation.

The two potential trends seen in the Ganymed data are both physical and are similar to those seen on Eros, though they are in terms of 2.9- μm band depth, not shape. The lack of potential observational trends in band depth or shape suggests that the variations in the 3- μm feature seen in observations of Ganymed are not due to observational circumstances. The spatial dependence indicated by the potential trend between the 2.9- μm band depth and sub-solar longitude might suggest all of Ganymed's H_2O (and/or OH and NH_3) came from a single impact, as the trend is roughly parabolic. De Sanctis et al. (2012) showed decreasing band depths on Vesta with increasing distance from areas of low albedo (Figure 3.18). Likewise on Ganymed, as the peak band depths occur around the relative 0° longitude, the point of impact would be located around that longitude. The asymmetry in the trend suggests the impactor hit Ganymed at an angle severe enough to scatter the carbonaceous or cometary material preferentially towards the east or that there is some topographic control of the ejecta that is unresolved in the lightcurve-based shape model. Current shape models of Ganymed do show what could be a sizable crater (Viikinkoski et al. 2017), but a model with more spatial resolution, along with an albedo map of similar resolution, is needed to confirm this hypothesis.

The potential trend in band depth with band I center on Ganymed shows band depth decreasing as band I center wavelength increases. Band I center is directly proportional to Fa and Fs content (Dunn et al. 2010), so a longer-wavelength band I center correlates to a higher percentage of fayalite and ferrosilite versus forsterite and enstatite, respectively. In other words, band depth decreases with increasing iron content (or equivalently increases with increasing magnesium content). Iron silicates have weaker chemical bonds than their magnesium counterparts due to iron's larger ionic radius, so it is possible that the volatile content on Ganymed's surface depends on mineralogical composition, or that the proposed impactor was

more magnesium-rich than the native composition of Ganymed's regolith. As with Eros, a space-based spectral and spatial study would be useful in testing these hypotheses.

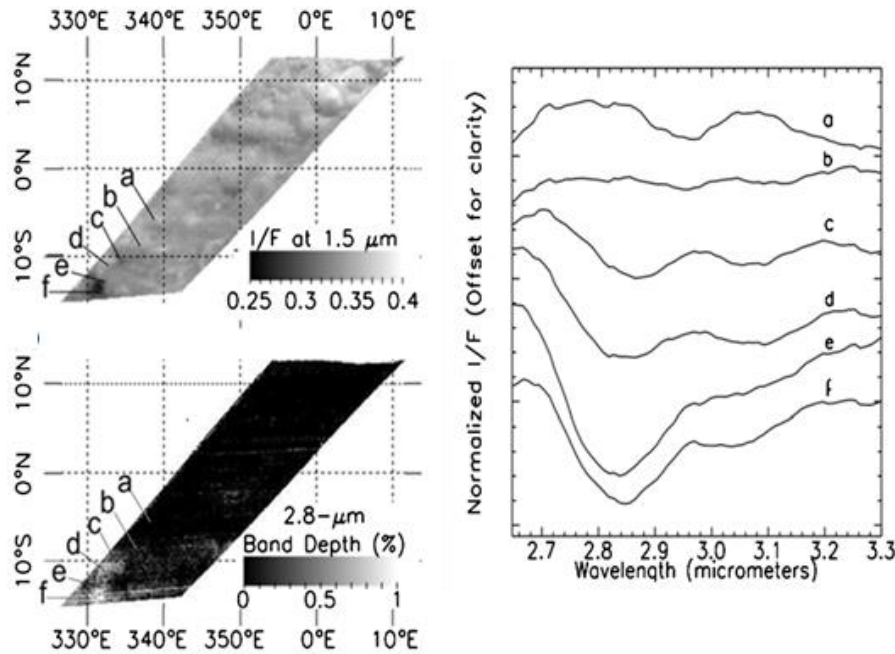


Figure 3.18: (Left) Section of Vesta's surface shaded by I/F (top) and 2.8- μm band depth (bottom). The darker area in I/F corresponds to a deeper band depth. (Right) Spectra corresponding to image on left, showing decreasing band depth as distance from impact increases. From De Sanctis et al. (2012).

3.5.3 Comparison to Other Datasets

As the two largest NEAs, both Eros and Ganymed have been the subject of previous ground-based studies, most notably by Rivkin et al. (2018) and Thomas et al. (2014). Rivkin et al. (2018), whose data has been included in this work, also investigated explanations for the variation in band depths seen in both of these asteroids. They identified a possible spatial trend in band depth for Eros, though theirs was in sub-observer longitude rather than latitude. Our data do not indicate such a trend, though localized areas of high OH content may exist (Figure 3.19). Rivkin et al. (2018) also detected a shallowly sloped negative trend in the 3.1- μm -to-2.95- μm reflectance ratio versus heliocentric distance for both Eros and Ganymed. Our data

exhibits either no trend or a shallow positive trend for Eros and Ganymed, respectively, which when combined with the Rivkin et al. (2018) data results in a shallower negative trend for Eros and a shallow positive trend for Ganymed (Figure 3.20). It is therefore unlikely that heliocentric distance affects the reflectance ratio, i.e., band shape, of either of these asteroids.

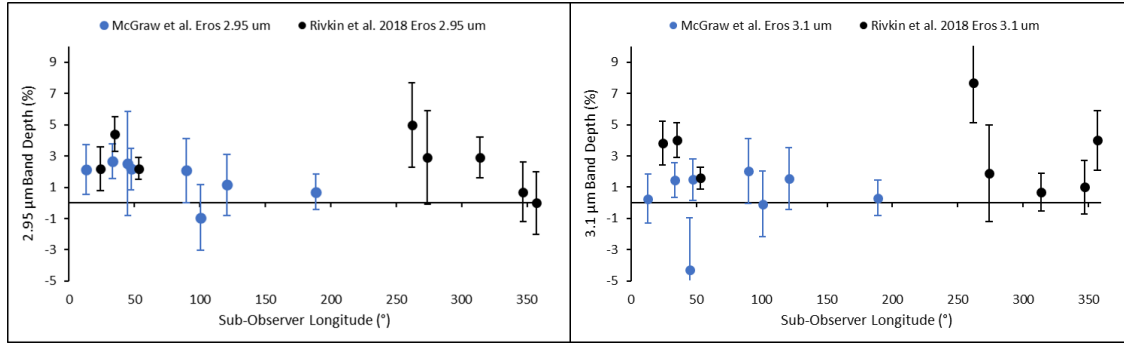


Figure 3.19: Band depth at 2.95 μm (left) and 3.1 μm (right) versus sub-observer longitude. Blue points represent observations made as part of this study and black points represent data from Rivkin et al. (2018). Band depth dependence with sub-observer longitude is not evident.

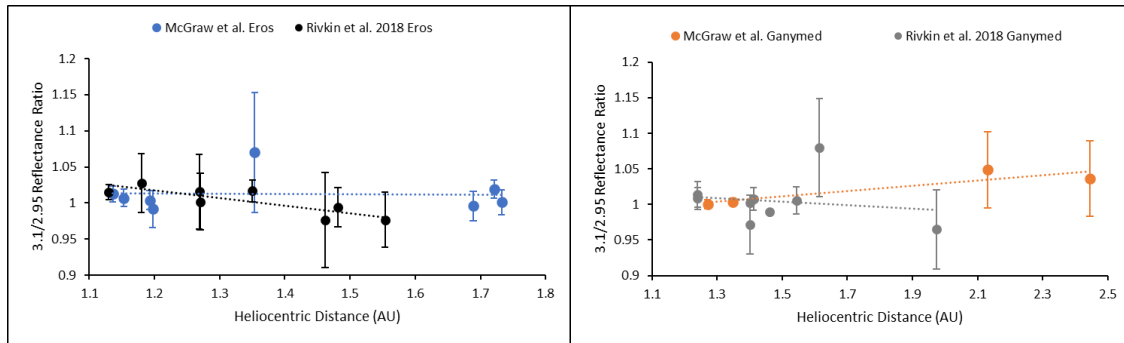


Figure 3.20: Ratio of reflectance at 3.1 μm to 2.95 μm versus heliocentric distance for Eros (left) and Ganymed (right). Blue and orange points and lines represent data collected during this study and black and grey points and lines represent data from Rivkin et al. (2018). Reflectance ratio dependence with heliocentric distance is not evident. Dashed lines represent best-fit linear trend.

Thomas et al. (2014) conducted a spectral survey of numerous NEAs using the IRTF's SpeX prism mode ($\lambda = 0.7\text{--}2.5 \mu\text{m}$), which included Eros and Ganymed. They reported a link between phase angle and both BAR and near-infrared slope (defined between $0.82 \mu\text{m}$ and $2.4 \mu\text{m}$) for both asteroids. The prism data presented here and in Thomas et al. (2014) are well-

matched for Eros in terms of BAR and phase angle, and likewise for Ganymed (Figure 3.21). However, in terms of NIR slope versus phase angle, our data for Ganymed matches those of Thomas et al. (2014), but for Eros we find a much shallower slope (Figure 3.21). In all cases, the trends in our dataset have the same sign as that seen by Thomas et al. (2014), confirming their hypothesis that phase reddening has occurred on both Eros and Ganymed. The cause behind the opposite slopes for Eros and Ganymed in BAR versus phase angle is as yet unclear.

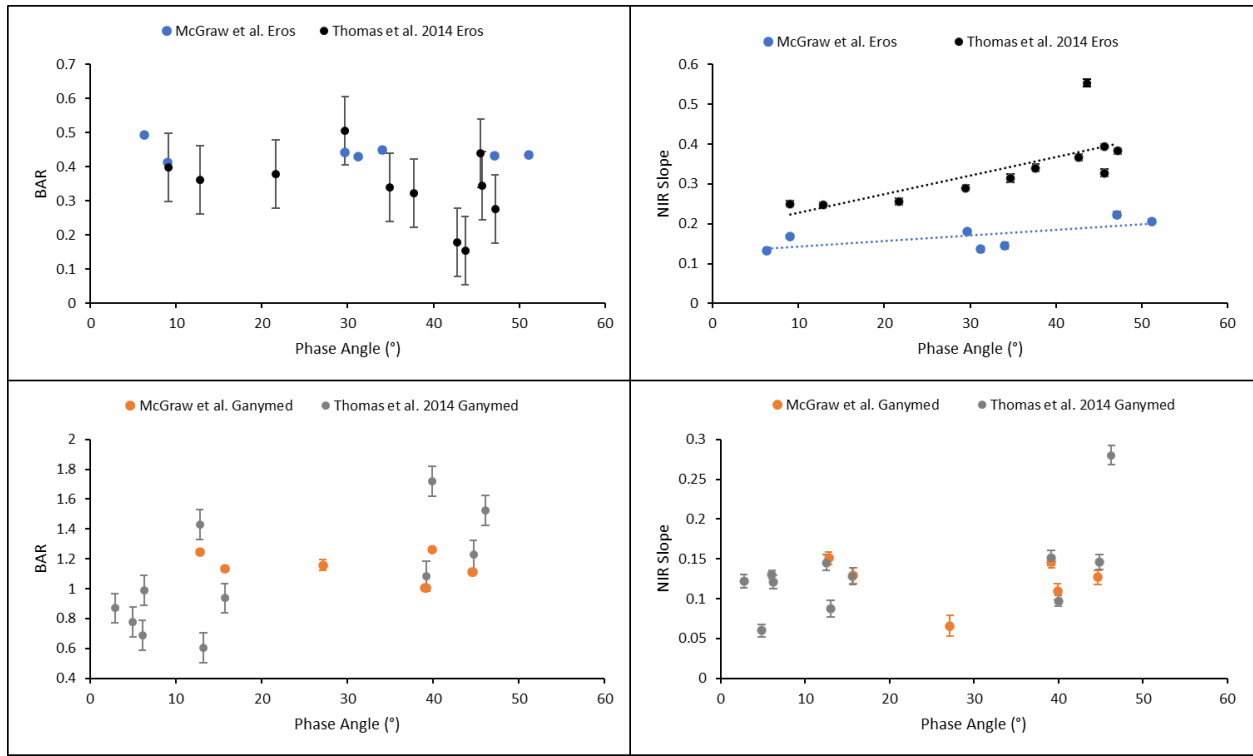


Figure 3.21: Plots of BAR vs. phase angle (left) and NIR slope vs. phase angle (right) for Eros (top) and Ganymed (bottom). Blue and orange points represent data from this study for Eros and Ganymed, respectively, and black and grey points represent data from Thomas et al. (2014) for Eros and Ganymed, respectively. Our data agrees with those of Thomas et al. (2014) except our NIR slope values are lower for Eros than Thomas et al. (2014) reported, as shown by the dashed, best-fit linear trend lines (black is Thomas et al. (2014) and blue is McGraw et al.).

3.5.4 (3122) Florence

The average band shape exhibited by Florence as observed on 3 September 2017 closely resembles the narrow bowl shape described by McGraw et al. (2022), so we agree with their hypothesis that Florence's surface has a mixture of OH and H₂O. In this scenario, the OH was delivered by solar wind hydrogen implantation and some was subsequently converted to H₂O by recombinative desorption (Orlando et al. 2018). As shown in Figure 3.12, Florence's band shape and depth vary across its surface, suggesting that the exact volatile composition and quantity vary as well. Starting at relative 0° longitude (Figure 3.12a), the wide bowl feature exhibited by Florence resembles that seen on Ganymed. This shape likely indicates that H₂O is the dominant species over OH. At 73° longitude (Figure 3.12d), the shape narrows, though it is still bowl-like, so the band at this longitude is also probably caused primarily by H₂O rather than OH. As Florence rotates to 143° (Figure 3.12b), the absorption feature begins to lose some of its roundedness and becomes more linear, similar to the average spectrum. A larger fraction of OH relative to H₂O is likely responsible for this shape. The final spectrum, at 290° longitude (Figure 3.12c), is best described as a wide linear feature, similar to the average Eros spectrum. Linear features such as this are typically attributed to OH (e.g., Takir & Emery 2012), so this portion of Florence's surface is dominated by OH rather than H₂O. Analyzing the band shape variations as a whole, as Florence rotates, the relative amount of OH increases and H₂O decreases, as the bowl-like shape of the band becomes more linear.

In terms of OH/H₂O quantity, the deepest band and therefore largest amount of OH/H₂O occurs at 143° longitude. However, the error bars are such that it is difficult to determine how the concentration changes across the surface. Estimating from the band depths and hydrogen concentrations found by De Sanctis et al. (2012; 2013), the relative range of hydrogen

concentration across Florence's surface is less than 40 ppm, not accounting for uncertainties. Though the volatile composition (i.e., OH-H₂O ratio) appears to change across Florence's surface, the total concentration of hydrogen on Florence is generally stable.

3.6 Summary and Conclusions

We observed the two largest near-Earth asteroids, (433) Eros and (1036) Ganymed, multiple times at different rotational phases and latitudes and compared our data to those previously published to determine the cause of variations in their 3- μ m O-H absorption bands (Rivkin et al. 2018; McGraw et al. 2022). We also analyzed rotationally resolved spectra of the NEA (3122) Florence collected by McGraw et al. (2022) to assess rotational variability in its OH/H₂O content. The eight spectra of Eros and six spectra of Ganymed, as well as the other spectra from Rivkin et al. (2018) and McGraw et al. (2022) discussed in this study, were collected using NASA's IRTF SpeX near-infrared spectrometer to further understand the source of OH/H₂O in near-Earth space.

The spectra of Eros and Ganymed have band shapes that suggest OH/H₂O compositions and sources that agree with those previously published. Eros' band, with depths of $-0.5 \pm 3.3\%$ to $8.7 \pm 6.3\%$, is typically shallow and linear, indicative of OH delivered via solar wind hydrogen implantation. No strong trends were identified to explain the variations in Eros' band depth and shape, but potential trends in band shape vs. sub-observer latitude and band I center suggest a spatial and/or compositional dependence. Ganymed's band depth ranges from $-0.6 \pm 1.5\%$ to $3.7 \pm 2.2\%$ and is typically shallow and rounded, indicative of H₂O, or potentially ammonia-bearing material, in addition to OH from exogeneous carbonaceous or cometary material. Only weak trends in band depth were discovered for Ganymed, but if real, the trends with sub-solar longitude and band I center suggest the hypothesized carbonaceous or cometary

impactor might have been more magnesium rich than the native regolith on Ganymed, and that it struck the surface near 0° relative longitude.

The average spectrum of Florence exhibits a $3\text{-}\mu\text{m}$ absorption feature that suggests its surface contains a mixture of OH delivered by solar wind hydrogen implantation and H_2O converted from OH by recombinative desorption, which as with Eros and Ganymed, agrees with previous published hypotheses. Florence's band depth ranges from $1.4 \pm 1.6\%$ at 0° relative longitude to $2.3 \pm 1.2\%$ at 143° relative longitude. As it rotates, Florence's band changes from rounded to linear, indicating the relative amount of H_2O decreases and OH increases in the regolith. The hydrogen concentration is fairly uniform across Florence's surface, even though the OH/ H_2O ratio is not. All three asteroids studied have OH/ H_2O with exogeneous origins and show a potential spatial dependence in $3\text{-}\mu\text{m}$ band depth and shape. If other bodies with non-native OH/ H_2O experience spatial variations in hydration, mapping out such variations across near-Earth space will further constrain exactly how OH/ H_2O is delivered and/or retained, which will help elucidate the source of terrestrial water and mechanisms by which it was delivered, as well as aid in resource utilization and planetary defense.

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4. A Case Study for 3- μ m Band Depth Variations: (101955) Benu

Abstract

Nominally anhydrous bodies are well-known to possess shallow features in the 2-4- μ m spectral region indicative of exogeneous OH/H₂O. One source of this material, solar wind hydrogen implantation, should be active on hydrated bodies as well, but the presence of a deep band and the absence of signal for ground-based observatories in this region has so far precluded a test of this hypothesis. I used data collected by NASA's OSIRIS-REx Visible and Infrared Spectrometer (OVIRS) of two sites on (101955) Benu to search for diurnal and annual band depth variations that would indicate the presence of a solar-wind-delivered component of Benu's 2.7- μ m hydration band. I found that both the mid-latitude boulder unofficially named Garuda and equatorial crater Alicanto experience diurnal and annual band depth variations generally consistent with solar orientation. It is likely that similar analyses of more sites on Benu would yield similar results and that solar wind hydrogen implantation is a common process acting on bodies in near-Earth space, regardless of native hydration.

4.1 Introduction

Numerous studies have detected volatiles such as hydroxide (OH) and water (H₂O), necessary components for a habitable world (e.g., Morbidelli et al. 2000), on seemingly anhydrous bodies in near-Earth space (e.g., Sunshine et al. 2009; Pieters et al. 2009; Clark 2009; De Sanctis et al. 2012; Rivkin et al. 2018; McGraw et al. 2022). The shallow absorption feature in the 2-4- μ m region indicative of surficial OH/H₂O (e.g., Benedict & Plyler 1951; Rivkin et al. 2002) evident on these nominally anhydrous bodies, such as the Moon (4) Vesta, and several near Earth Asteroids (NEAs) including (433) Eros and (1036) Ganymed, is linked to solar wind hydrogen implantation and exogeneous carbonaceous and/or cometary material. These processes

should also be active on nominally hydrous bodies, such as many asteroids in the C-complex, but the presence of a relatively deep band ($> 5\%$) due to native phyllosilicates (e.g., Brearley & Jones 1998) generally precludes any further study into the source of the OH/H₂O detected. Additionally, ground-based observations are insufficient to determine if a secondary source of OH/H₂O is present on a target that also has mineralogical OH/H₂O. Unbound exogeneous OH/H₂O is linked to a shallow feature in this region with a band minimum around 2.8 μm (e.g., Pieters et al. 2009), a slightly longer wavelength than that for native Mg-rich phyllosilicates (i.e., $\sim 2.7 \mu\text{m}$; Hamilton et al. 2019). Nearly 100% of the radiation between 2.55 μm and 2.85 μm is absorbed by atmospheric water vapor when using a telescope on Earth, obscuring the center of the band and precluding OH/H₂O source identification. A detailed space-based campaign of an object is required to assess whether any component of its deeper 2-4- μm band is attributable to a secondary delivery mechanism, such as solar wind hydrogen implantation.

One such object, the near-Earth asteroid (101955) Bennu, was the target of NASA's Origins, Spectral Interpretation, Resource Identification, and Security-Regolith Explorer (OSIRIS-REx) mission (Lauretta et al. 2017). Bennu is a B-type asteroid and exhibits a global hydration feature with a band minimum at $2.74 \pm 0.01 \mu\text{m}$ (Hamilton et al. 2019) that has depths of 12-17% (Simon et al. 2020b), significantly deeper than the $< 5\%$ band depths seen on nominally anhydrous bodies (e.g., Sunshine et al. 2009; Pieters et al. 2009; Clark 2009; De Sanctis et al. 2012; Rivkin et al. 2018; McGraw et al. 2022). The abundant observations of Bennu made at different points in its orbit and at different times during its local day allow for a detailed temporal study of Bennu's 2.7- μm feature in order to detect any potential band depth and shape variations. Such variations might be caused by solar wind hydrogen implantation, a mechanism with a temporal component, as seen on the Moon (e.g., Sunshine et al. 2009; Wöhler

et al. 2017; Laferriere et al. 2022). Though some studies seem to disprove the apparent diurnal variations in hydration band depth detected in lunar spectra (e.g., Ruiz et al. 2020), they used data that did not cover the entire band thereby assuming a band depth and shape when thermally modelling the long-wavelength portion of the spectra. The data in which diurnal variations were evident have complete coverage of the band, thus allowing the band depth and shape to be generally independent of the thermal model parameters. The potential ubiquity of this process in near-Earth space could at least partially explain how water was delivered to Earth.

4.1.1 Bennu in the Near Infrared

OSIRIS-REx launched in September 2016 with the primary goal of collecting and returning a sample from Bennu (Table 4.1), a near-Earth asteroid (NEA) whose carbon-rich, primitive regolith will help answer questions regarding planetary formation (e.g., Laurretta et al. 2017). Bennu is a very dark ($A = 0.021\text{-}0.027$; Zou et al. 2021) rubble pile asteroid with a rough and

rocky surface covered in meter-sized boulders (DellaGiustina et al. 2019; Walsh et al. 2019; Jawin et al. 2020). It exhibits a shallow blue-slope in the near-infrared (NIR) and global $2\text{-}4\text{ }\mu\text{m}$ features indicative of OH/H₂O- and carbon-bearing minerals (e.g., Hamilton et al. 2019; Simon et al. 2020b; Ferrone et al. 2021; Kaplan et al. 2021). The deep, sharp band at $2.74\text{ }\mu\text{m}$ is caused by hydroxide bound in phyllosilicate minerals, likely magnesium-bearing (Simon et al. 2020a), and exhibits only minor depth variations across Bennu’s surface. These minor variations are primarily linked to morphological features (e.g., Barucci et al. 2020; Praet et al. 2021) and latitude (Simon et al. 2020b). The NIR spectral shape exhibited by Bennu, along with its average

Table 4.1: Properties of (101955) Bennu

Spectral Type	B-type
Diameter	482 m
Geometric Albedo	0.044
Perihelion	0.897 au
Aphelion	1.356 au
Rotation Period	4.296 hrs
Orbital Period	1.20 yrs
Orbital Inclination	6.03°
Orbital Eccentricity	0.204
Axial Tilt*	177.6°

**From Laurretta et al. (2017), all others from JPL Horizons*

hydrogen content of 0.71 ± 0.16 wt% (Praet et al. 2021), suggests that Bennu is most closely associated with CM and CI meteorites (e.g., Hamilton et al. 2019; Praet et al. 2021), though it likely originated in the inner Main Belt in the v_6 region (Bottke et al. 2015; Granvik et al. 2018; Moskovitz et al. 2022). The possibility of solar wind hydrogen implantation as a secondary contributor to the 2.7- μm feature has been hypothesized (Brunetto et al. 2020; Praet et al. 2021), but a detailed investigation has yet to be conducted. Most work on the 2.7- μm band has only used one spectral dataset, that collected on 9 May 2019 at a local solar time of 12:30 (Equatorial Station 3), as it was collected at peak solar illumination (e.g., Barucci et al. 2020; Simon et al. 2020b; Simon et al. 2020a; Praet et al. 2021; Praet et al. 2023). Previous work has not compared data from multiple times of day or year.

4.1.2 Hydroxide and Water in Near Earth Space

Four main sources of OH/H₂O have been hypothesized for airless bodies. (1) Carbonaceous impacts are responsible for hydration absorption features on (4) Vesta (e.g., McCord et al. 2012; DeSanctis et al. 2012) and likely on the NEA (1036) Ganymed (McGraw et al. 2022), while (2) cometary impacts might have delivered water to the Moon and Mercury (e.g., Greenwood et al. 2011; Neumann et al. 2013). The Main Belt is approximately 21-30% phyllosilicates by mass (Brearley & Jones 1998), making (3) native phyllosilicates a major source of OH/H₂O, though only about 15% of NEAs are expected to have them (Binzel et al. 2019). The final source, (4) solar wind hydrogen implantation (e.g., Zellner et al. 1966; Starukhina 2001), is believed to have delivered OH/H₂O to the Moon (e.g., Sunshine et al. 2009) and some NEAs such as (433) Eros and (3122) Florence (Rivkin et al. 2018; McGraw et al. 2022).

These sources can generally be distinguished by analyzing the depth and shape of the

hydration feature in the 2-4- μm spectral region, the location of a fundamental stretching vibration between oxygen and hydrogen (e.g., Benedict & Plyler 1951). Deep absorption features are generally associated with OH/H₂O bound in mineral structures compared to shallow features that are more typically linked to unbound, surficial molecules in smaller quantities (e.g., Pieters et al. 2009). The band shape and minimum are used to determine exact composition (e.g., Rivkin et al. 2002). Sharp, linear bands are typically associated with OH while bowl-like features indicate H₂O (e.g., Rivkin & Emery 2010; Takir & Emery 2012; Rivkin et al. 2019). Other factors can be used to further constrain the OH/H₂O source. For example, dark craters can be linked to exogenous carbonaceous and/or cometary material, such as seen by Dawn on Vesta (e.g., Prettyman et al. 2012; McCord et al. 2012; Reddy et al. 2012; DeSanctis et al. 2012). A second example is that solar wind hydrogen implantation is potentially temporally dependent, as the band depth on the Moon appears to vary with solar orientation (Sunshine et al. 2009).

The deep, sharp feature present on Bennu signifies hydroxide bound in native phyllosilicates is the dominant source of OH/H₂O, rather than water or unbound hydroxide. Additionally, given that the surface of Bennu is generally homogenous in terms of albedo and 2.7- μm band depth (e.g., Barucci et al. 2020; Praet et al. 2021; Zou et al. 2021), exogenous carbonaceous and/or cometary material is unlikely. Analyzing the spectra of Bennu for potential annual and/or diurnal variations is required to determine if any component of its 2.7- μm band can be attributed to hydrogen delivered via the solar wind.

4.2 Methods

4.2.1 Selection of Study Sites

Two locations were selected on which to test the hypothesis that a component of Bennu's 2.7- μm feature is due to solar wind hydrogen implantation. The first region of interest (ROI) is a

rock unofficially named “Garuda” that is located in Tlanuwa Regio at 262.88E -38.72 (Figure 4.1). It was selected as an initial review showed it possessed a slightly deeper 2.7- μm feature than its surroundings though later work showed it has a shallower band than the global average for Bennu. The second ROI is the 60-km wide Alicanto crater near the equator (centered at 111.93E -0.08; Figure 4.1). It was selected as a counterpoint to the first ROI to determine how the solar wind affects equatorial regolith in comparison to a lower-latitude monolith.

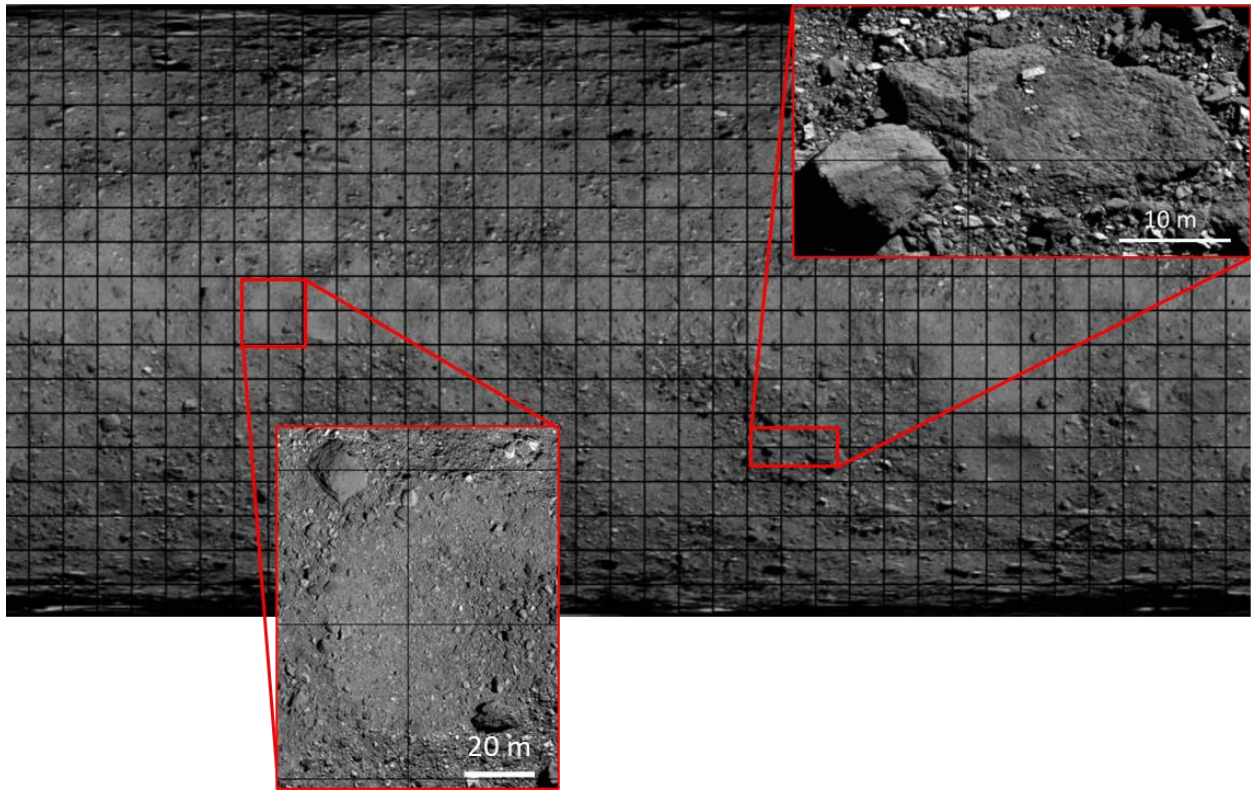


Figure 4.1: Projection of (101955) Bennu overlaid by close-up views of Alicanto (left) and Garuda (right), the two regions of interest for this study.

4.2.2 Data Selection & Acquisition

The data used in this study was collected by the OSIRIS-REx Visible and IR spectrometer (OVIRS). OVIRS produces spectra with wavelengths between 0.4 μm and 4.3 μm and $R \geq 200$ in the 2- to 4- μm range (Reuter et al. 2018). I primarily used data from the Detailed Survey phase of the OSIRIS-REx mission (Table 4.2; Lauretta et al. 2017). This phase of the mission was comprised of two parts, the Baseball Diamond (BBD) and Equatorial Stations (EQS). The Baseball Diamond phase consisted of seven flybys conducted between 7 March 2019 and 19 April 2019. OVIRS was not a primary instrument on any of the flybys but did collect data during the first three flybys, as well as on the refly of Baseball Diamond station 2 on 26 September 2019. Data from Baseball Diamond flybys 1, 3, and 2 refly are included in this work; BBD2 did not contain data of our sites of suitable quality.

Table 4.2: Detailed Survey Stations used in this study

Station Name	Station Acronym	Date	Heliocentric Distance (au)	Nominal Local Solar Time
Baseball Diamond 1	BBD1	7-Mar-2019	0.996	12:30
Baseball Diamond 3	BBD3	21-Mar-2019	1.041	10:00
Equatorial Station 1	EQS1	25-Apr-2019	1.158	15:00
Equatorial Station 3	EQS3	9-May-2019	1.201	12:30
Equatorial Station 4	EQS4	16-May-2019	1.221	10:00
Equatorial Station 5	EQS5	23-May-2019	1.239	6:00
Baseball Diamond 2 Refly	BBD2-refly	26-Sep-2019	1.329	12:30
Bennu Final Flyby	BFF	7-Apr-2021	0.994	12:30

The Equatorial Station phase occurred from 25 April 2019 to 6 June 2019 and consisted of seven stations (15:00, 03:20, 12:30, 10:00, 06:00, 20:40, and 18:00 LST, respectively). For these stations, OVIRS scanned North to South across the asteroid and was primarily nadir-pointed East-West. OVIRS was a primary instrument at all seven stations, but I only used data

from stations 1 (15:00), 3 (12:30), and 4 (10:00) due to lack of sunlight on the other stations. I also used data collected during EQS5 (06:00) for Alicanto, as some observations were made with OVIRS pointed off-nadir E-W by 2.5 hours sunward (i.e., at 08:30 LST). Finally, I used data from the Bennu Final Flyby (BFF), which occurred on 7 April 2021 and repeated the observations made during the 12:30 LST equatorial station (EQS3). I used J-Asteroid, an imaging package based on JMARS (Christensen et al. 2009), to select OVIRS frames that covered each ROI. I only used stamps for which at least half their area was the ROI (Figure 4.2) and those whose field of view was filled by the asteroid.

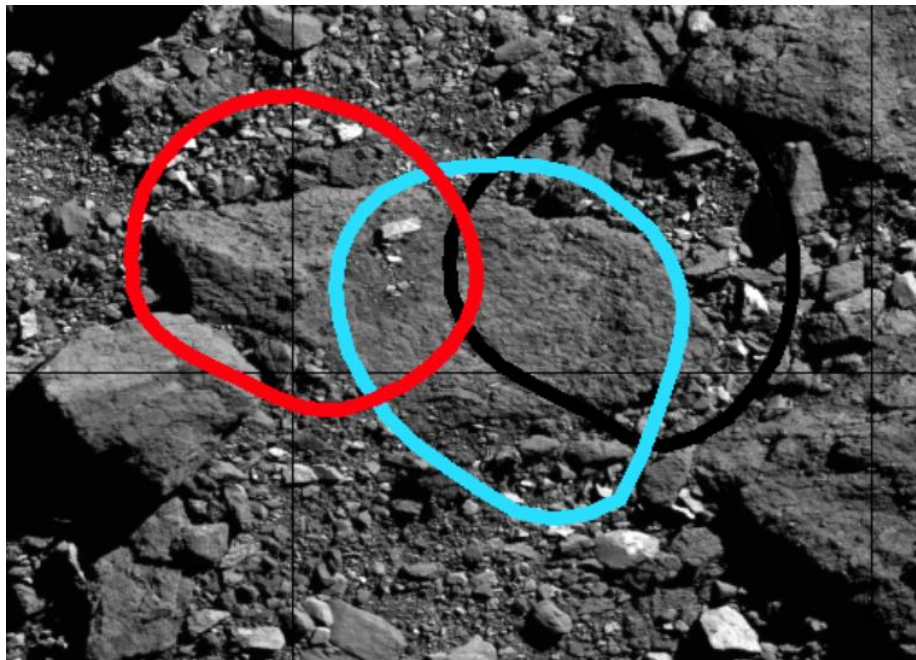


Figure 4.2: Example of spots whose area is at least half filled by the ROI. This example is the spots for Garuda from Equatorial Station 3 (12:30 LST).

4.2.3 Data Processing

The data went through several processing steps and each step is identified by a level number (Table 4.3; Simon et al. 2021). I used level 3 data, which is irreversibly processed from the calibrated data (level 2) and, for OVIRS, has several derived products. I started with radiance data that had been resampled to the correct wavelengths; this is the lowest level 3 dataset and is

known as level 3a. The L3a data downloaded from the SpocFlight database still contains a thermal component that affects the 2-4- μm spectral region. A higher-level data product, level 3b (and above), removes the thermal tail such that only the reflected component remains. The thermal tail is removed from each spectrum by fitting a single-temperature blackbody curve to the isolated thermal radiance spectrum and subtracting that smoothed curve from the radiance spectrum (Simon et al. 2020b). However, the official thermal tail removal (TTR) code offered by the mission pipeline does not adequately model the spectral region of interest for some spectra in the detailed survey stations, so a custom TTR was used.

Table 4.3: OSIRIS-REx Data Levels

Data Level	Description
0	Raw instrument data reconstructed from telemetry
1	Uncalibrated data
2	Data calibrated to units proportional to physical units
3	Irreversibly processed higher-level products from a single source
3a	Calibrated and resampled radiance spectra in units of $\text{W}/\text{cm}^2/\mu\text{m}/\text{sr}$ per spectral element
3b	L3a radiance spectra with the estimated thermal contribution removed
3c	L3b radiance spectra divided by the range-corrected solar flux, in units of I/F
3e	L3c I/F spectra photometrically corrected to REFF (reflectance factor) at a viewing geometry of 30° incidence angle, 0° emission angle, and 30° phase angle
3radf	L3e REFF spectra converted to RADF (radiance factor, units equivalent to I/F) at a viewing geometry of 0° emission, incidence, and phase angles
3f	Bolometric albedo values
3g	Spectral Indices (mineral and chemical identification)
4	Data derived by combining data from more than one source

Data collected when the OVIRS detector and/or Bennu's surface were at higher temperatures, such as was the case during BBD1, BBD3, and BFF, suffer from detector non-linearity and saturation at longer wavelengths. The pipeline TTR fit range includes longer

wavelengths than the custom TTR, so produces a poorer estimate of the thermal tail in these cases. The 2.7- μm band shape is affected by the removal of the thermal tail, and by fitting to slightly shorter wavelengths, I am able to perform a better TTR for these data. This custom TTR uses the continuum from a shorter wavelength than the pipeline TTR to remove the thermal component, which allows the 2.7- μm hydration feature to be preferentially modelled at the cost of the longer-wavelength ($\lambda > 3.5 \mu\text{m}$) data. The baseball diamond and final flyby data are the most affected by TTR code choice while the equatorial station data is relatively unaffected (Figure 4.3). Though non-linearity in some spectra even with the custom TTR could affect the shape of the 2.7- μm band, particularly at longer wavelengths, the shorter wavelengths including the band center are largely unaffected and considered reliable for this study. Along with removing the thermal tail, the custom TTR code divides by the solar flux spectrum, converting the L3a radiance data into reflectance data equivalent to the L3c data. I did not apply a photometric correction as data directly compared together have similar emission angles (Alicanto emission angles $\approx 15^\circ$; Garuda emission angles $\approx 35^\circ$).

4.2.4 Temporal Analysis

I calculated an average spectrum at each ROI for each flyby/station/LST. The spectra included in each average generally possess the same shape and depth (Figure 4.4). Any

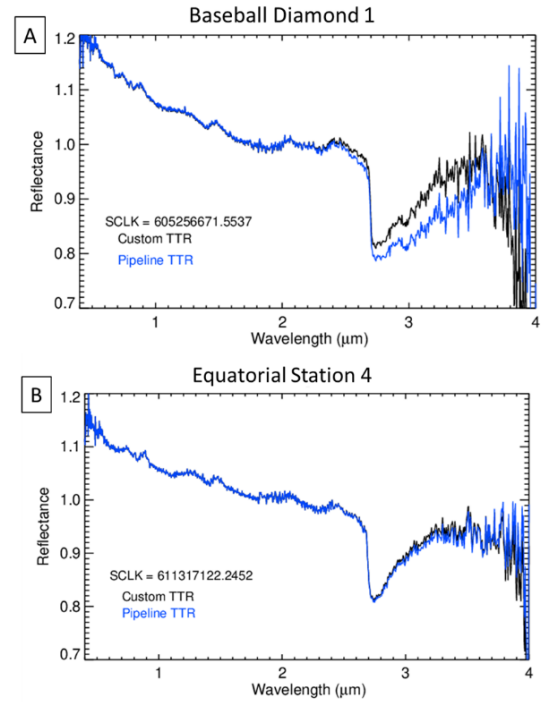


Figure 4.3: Example spectra of Garuda using the custom TTR (black) and the pipeline TTR (blue) from Baseball Diamond 1 (A) and Equatorial Station 4 (B).

variations in band depth and/or shape between stations is therefore due to diurnal or annual effects, given the low inherent variability in the individual spectra. These averages were ratioed against each other to enhance any differences between the spectra; the base spectrum (i.e., the spectrum ratioed against itself to produce a line of unity) and those ratioed against it depends on the specific temporal comparison. Both Alicanto and Garuda were observed across enough stations to conduct both time of day (ToD) and time of year (ToY) studies. The ToD studies only utilized data from the equatorial stations to study any diurnal differences in 2.7- μm band depth and shape. I then compared the averages of data taken at the same local solar time but on different dates (i.e., EQS3 and BFF for 12:30 LST) to assess any annual band depth and shape variations.

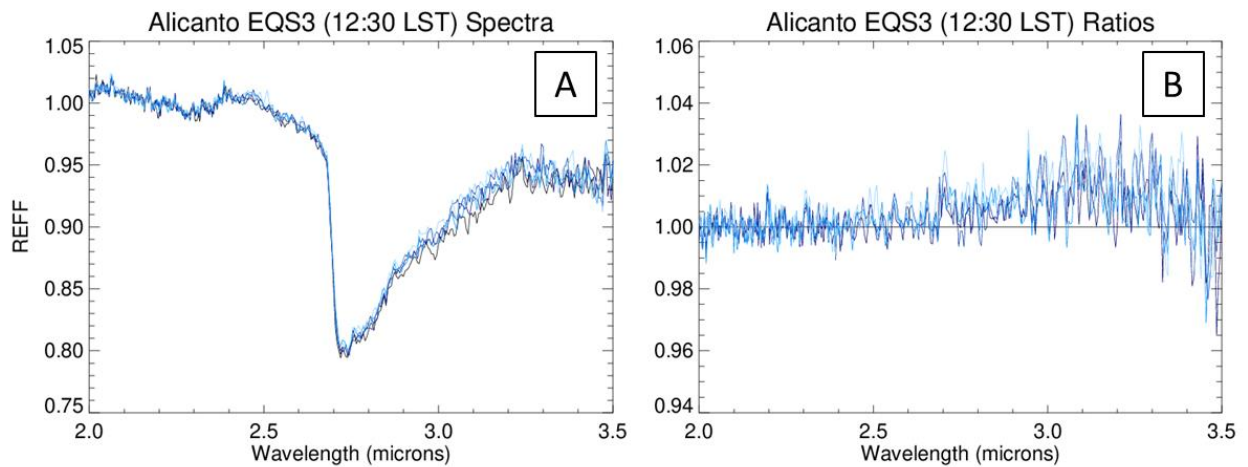


Figure 4.4: (A) Five example spectra of Alicanto from Equatorial Station 3 (12:30 LST) and (B) ratios of those spectra showing low inherent variability.

4.3 Results & Analysis

4.3.1 Garuda

The frames used in each spectral average for Garuda are listed in Appendix B (Table B.1). Three temporal comparisons were made for Garuda: one diurnal and two annual. The

diurnal comparison used data from EQS1 (15:00 LST), EQS3 (12:30 LST), and EQS4 (10:00 LST; Figure 4.5a & b). The 2.7- μm band is deepest at 12:30 LST and shallowest at 15:00 LST, though the spectrum at 15:00 LST also has the largest point-to-point spread. The 10:00 and 12:30 LST spectra have nearly identical band shapes, as both exhibit a shoulder or inflection point at approximately 2.86 μm . The 15:00 LST spectrum instead has a potential inflection point around 2.98 μm , though the relatively low signal-to-noise ratio (S/N) makes the shape difficult to determine.

Annual comparisons were made at 10:00 LST and 12:30 LST. The 10:00 LST annual study used data from BBD3 and EQS4 (Figure 4.5c & d). The BBD3 spectrum has the shallowest 2.7- μm band, though a secondary absorption feature at ~ 2.99 μm that the EQS4 spectrum lacks makes it the shallowest band at longer wavelengths. Two stations, EQS3 and BFF, collected data at 12:30 LST. The BFF spectrum has a deeper, blockier band than the EQS3 spectrum (Figure 4.5e & f). The BFF spectrum also shows higher reflectance values than the EQS3 spectrum from approximately 2.49 μm to 2.69 μm and from approximately 3.14 μm to 3.41 μm .

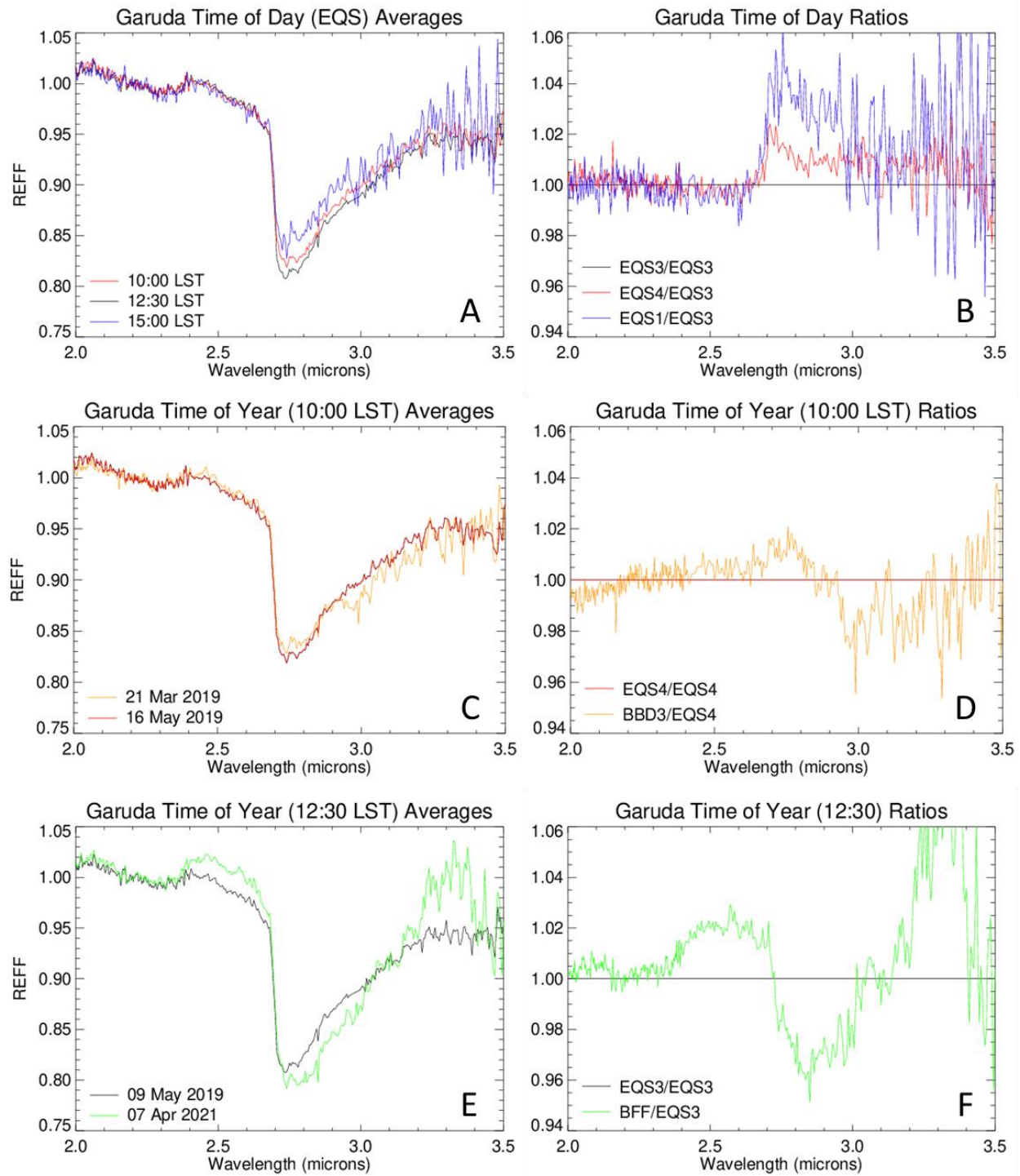


Figure 4.5: Diurnal and annual spectral averages and ratios for Garuda.

4.3.2 Alicanto

The frames used in each spectral average for Alicanto are listed in Appendix B (Table B.2). Three temporal comparisons were also made for Alicanto, one diurnal and two annual, and the data for these comparisons generally have a smaller point-to-point spread than those used for Garuda. The diurnal comparison used data from four stations: EQS1, EQS3, EQS4, and EQS5 (Figure 4.6a & b). The EQS5 station primarily took data at 6:00 LST, but I used the data collected at 8:30 LST during this orbit. All four spectra show similar band shapes, with an inflection point at approximately $2.86\ \mu\text{m}$ that was also seen in the 10:00 LST and 12:30 LST Garuda spectra. The inflection is weaker for the 15:00 LST spectrum though still evident. Also as with Garuda, the deepest $2.7\text{-}\mu\text{m}$ band occurs at 12:30 LST and the shallowest at 15:00 LST, though the 8:30 LST is similarly shallow.

Annual comparisons for Alicanto were made at the same times as for Garuda. Stations BBD1 and EQS4 were used to make the 10:00 LST comparison (Figure 4.6c & d). The spectrum from EQS4 has a slightly deeper band than that from BBD1, but both spectra have nearly identical $2.7\text{-}\mu\text{m}$ band shapes. As shown by Figure 4.6d, these spectra are the most similar out of all spectra compared in this project. Four stations collected data at 12:30 LST: BBD1, EQS3, BBD2-refly, and BFF (Figure 4.6e & f). All four spectra have similar $2.7\text{-}\mu\text{m}$ band depths, though bands from BBD1 and BBD2-refly are slightly deeper than those from EQS3 and BFF. Using the ratio plot for these spectra (Figure 4.6f) shows the BFF spectrum is the shallowest. The EQS3, BBD2-refly, and BFF spectra have similar band shapes, though the BFF spectrum has higher reflectance values at wavelengths shorter and longer than the band as on Garuda. The BBD1 spectrum lacks the inflection at $\sim 2.86\ \mu\text{m}$ shown in the other spectra but has the same secondary absorption feature at $\sim 2.99\ \mu\text{m}$ as seen in the BBD3 data for Garuda.

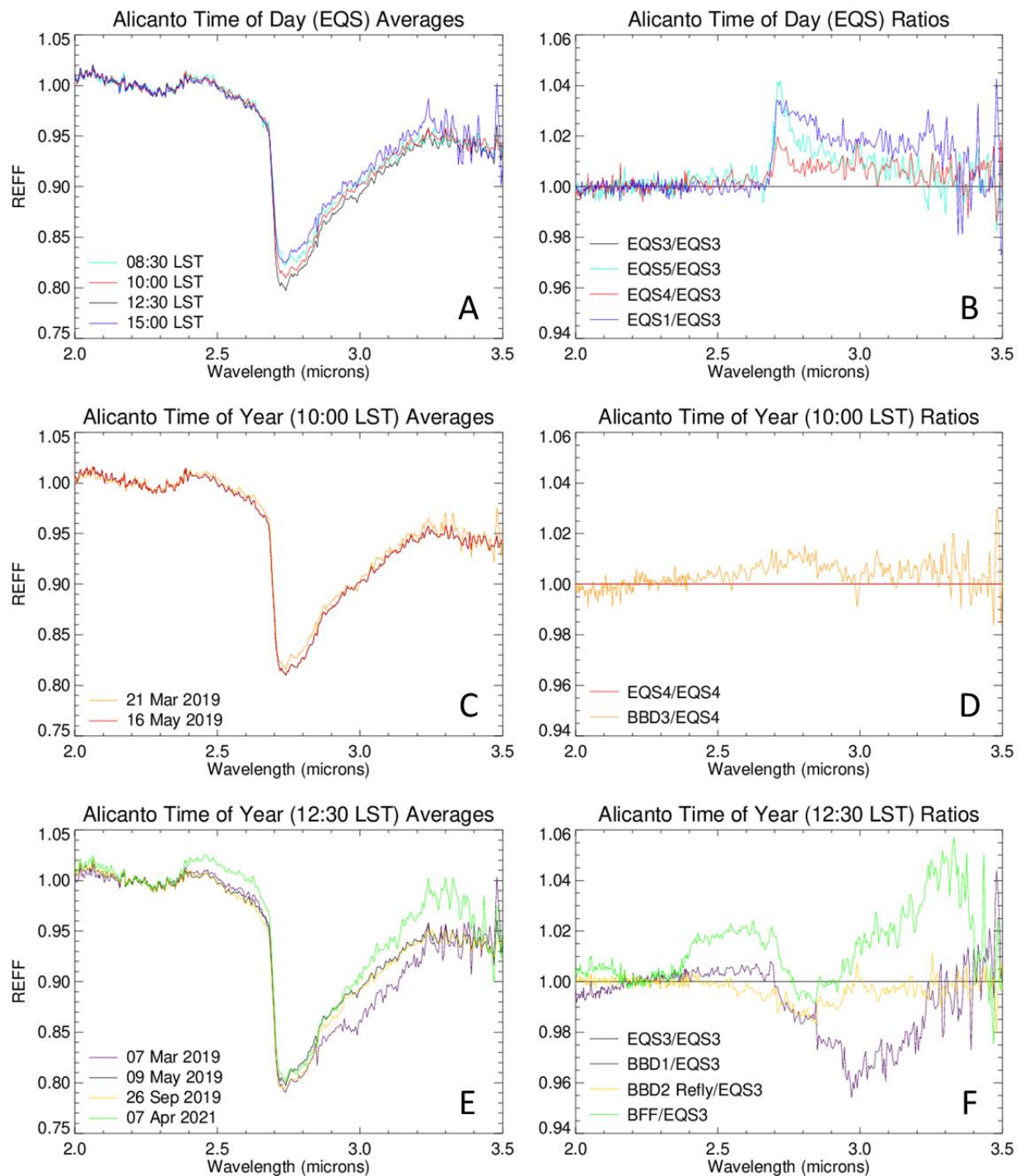


Figure 4.6: Diurnal and annual spectral averages and ratios for Alicanto.

4.4 Discussion

4.4.1 Diurnal Variations

Diurnal 2.7- μm band depth variations are evident at both study sites on Bennu. As native phyllosilicates should not cause a temporally variable band, a secondary OH/H₂O source is likely. Given that the variations seen on Bennu are of similar magnitude to band depth variations present on other NEAs, such as (433) Eros and (1036) Ganymed (see Section 3 of this study; Rivkin et al. 2018), similar delivery mechanisms are likely active on these bodies. Exogenous carbonaceous or cometary material, as is likely present on Ganymed, should also not vary temporally, suggesting solar wind hydrogen implantation is the secondary source of OH/H₂O on Bennu. For both Garuda and Alicanto, the deepest band occurs at 12:30 LST (EQS3) and the shallowest at 15:00 LST (EQS1), though Alicanto's band at 08:30 LST (EQS5) is almost as shallow. The station with the most direct solar illumination was EQS3 (12:30 LST), so this station also had the most incident solar wind. It might therefore be expected that, if a component of Bennu's 2.7- μm absorption feature was due to solar wind hydrogen implantation, then the deepest band would occur at 12:30 LST as the implanted hydrogen ions would add to the native hydrogen content from phyllosilicates. Similarly, it would be expected for bands to shallow as the time difference from 12:30 LST increases. Such is the case on Bennu, as the 08:30 LST and 15:00 LST bands are shallower than the 10:00 LST band.

The relationship between 2.7- μm band depth and local solar time on Bennu is opposite to that seen on the Moon (Sunshine et al. 2009; Laferriere et al. 2022). Data collected by NASA's Deep Impact mission showed a global, shallow 2.8- μm absorption feature that was deepest in the morning and evening and shallowest at noon. Sunshine et al. (2009) hypothesized that OH/H₂O was delivered during the entire day, but it photodissociated as solar illumination increased.

Bennu's inverse relationship could be explained in multiple ways. First, it is possible that the presence of native, bound OH helps prevent photodissociation of the OH/H₂O delivered via the solar wind, thereby making it more stable than the same species on the Moon. The exogenous OH/H₂O might be more strongly bound than it would be on a nominally anhydrous surface. Phyllosilicate chemical structures are significantly more complex than those of common minerals on nominally anhydrous surfaces (e.g., olivine and pyroxene). Complex crystal structures allow for more defects and extra ions than simple structures, providing ample opportunity for incoming hydrogen ions to interact with bound oxygen atoms. Additionally, the Moon's equilibrium temperature, which approximates the surface temperature for airless bodies, is approximately 30% higher than that of Bennu during the equatorial station phase of the mission. If Bennu's surface temperature is low enough to preclude photodissociation of OH/H₂O, then the time of peak solar illumination, and therefore peak solar wind impact, would correlate with deeper bands for Bennu even though that time resulted in the shallowest bands on the Moon. Finally, the lunar day is much longer than Bennu's, resulting in about 14 Earth days of illumination compared to only 2.15 hours for Bennu. OH/H₂O creation and retention timescales are dependent on the diffusion properties of the surface as well as the activation energy to form OH/H₂O. Low activation energies can result in rapid (i.e., < 1 s) OH/H₂O loss (Farrell et al. 2017), so Bennu's short day does not necessarily preclude solar wind hydrogen implantation as a cause of the observed diurnal variations. These vastly different rotation rates could also affect the diurnal variations in band depth, as the lunar surface is warming for longer than Bennu, which gives OH/H₂O more time to form and then photodissociate. Bennu's lower surface temperature, faster rotation rate, and/or more hydrated composition relative to the Moon could be responsible for the same OH/H₂O delivery mechanism producing opposing trends on different bodies.

4.4.2 Annual Variations

Annual variations in 2.7- μm band depth are also evident on Bennu at both study sites, though are not as distinct. At 10:00 LST, the spectra collected during BBD3 have the shallowest absorption feature for both Garuda and Alicanto. OSIRIS-REx was closer to the Sun during BBD3 than during EQS4 (Table 4.2), so it might be expected for BBD3 to have the deeper band as the solar wind particle density is roughly proportional to the inverse square of heliocentric

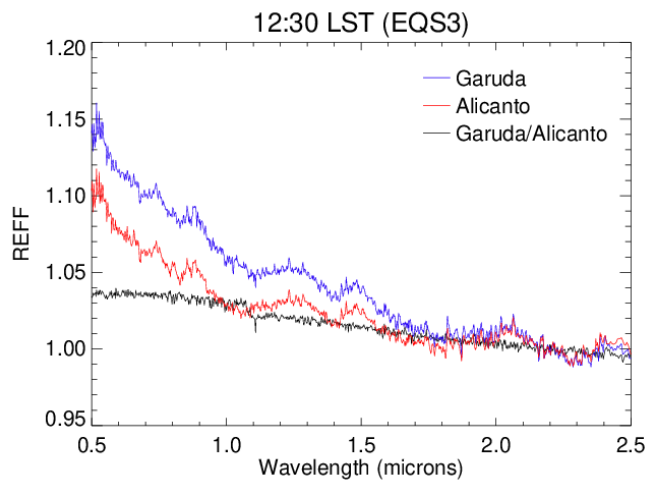


Figure 4.7: Spectra of Garuda (blue) and Alicanto (red) from 0.5 to 2.5 μm at 12:30 LST from EQS3. Both sites have similar spectral shapes indicating similar compositions. A ratio of the two spectra is in black.

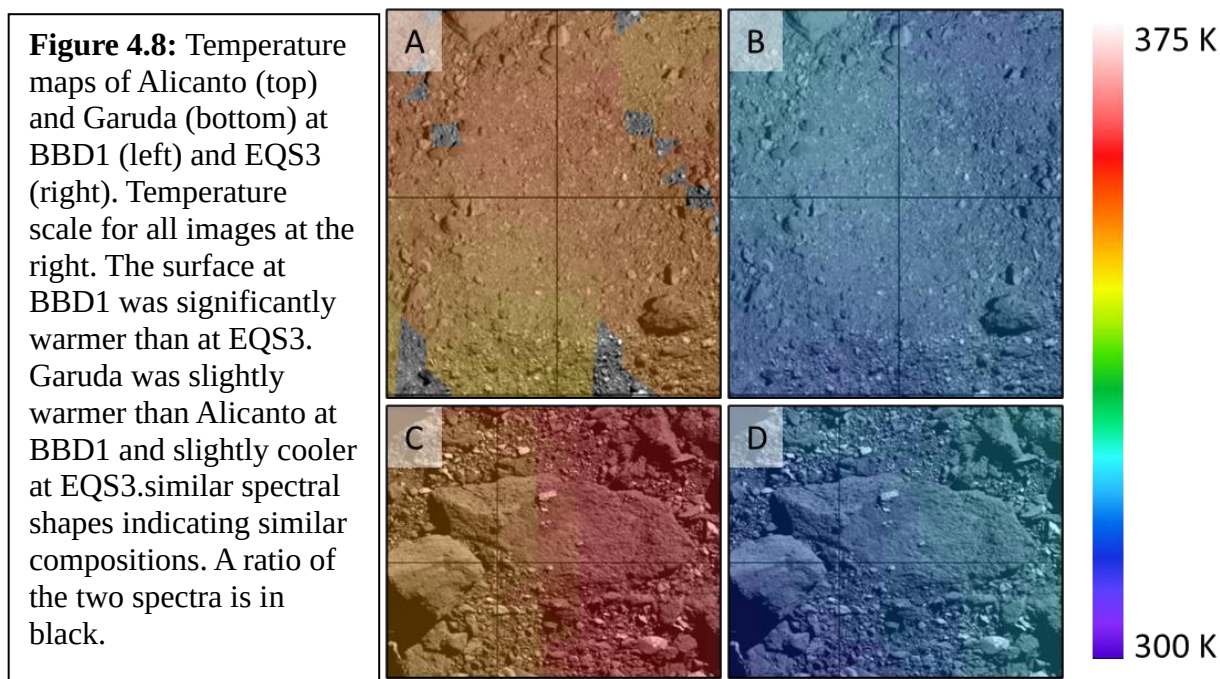
distance (e.g., Elliott et al. 2019). Something besides heliocentric distance must be responsible for the observed trend. The band depth differences at 10:00 LST are smaller than in any other comparison, so it is possible that the annual variation is simply a result of observing parameters and data quality (see Section 4.4). Analyzing more sites on Bennu’s surface and including more 10:00 LST data will help explain this variation.

At 12:30 LST, the relationship between station and band depth for the two sites varies. At Garuda, the deepest band is from the BFF dataset, when Bennu was closer to the Sun than at any other time in the dataset used in this study. This station therefore experienced the highest particle density, so it would be expected for the station with the lowest particle density, EQS3, to have the shallowest band, which it does. The trend in heliocentric distance and band depth seen at

Garuda for this local solar time is absent at Alicanto, as the BFF and EQS3 data show similar depths, both of which are shallower than the BBD1 and BBD2-refly bands. The different behavior between the two sites suggests a latitudinal dependence on solar wind interaction, as grain size or compositional effects are unlikely. Smaller grains would generally cause a unilateral decrease in band depth (e.g., Lin et al. 2020; Sun & Lucey 2022) regardless of heliocentric distance or illumination angle, and Garuda and the regolith in Alicanto are the same composition (Figure 4.7).

4.4.3 Low versus Mid-Latitudes

Garuda and Alicanto behaved similarly over the course of one day, indicating latitude does not control the diurnal band depth variations that are likely due to solar wind hydrogen implantation. However, latitude may be important in understanding the annual variations in band depth, given the different patterns in spectral behavior at 12:30 LST seen at the two sites studied. Alicanto should and does experience less annual disparity due to its low latitude. The band depth



variations are greater for Garuda than Alicanto, indicating that Alicanto's band depth is more stable throughout the year. Additionally, Garuda experiences greater temperature swings, as during BBD1 Garuda was slightly warmer than Alicanto but was slightly cooler during EQS3 (Figure 4.8). The apparent minor band depth variations seen at Alicanto at 12:30 LST may be more indicative of different observing parameters, like at 10:00 LST (Section 4.2), than a physical cause. Conducting annual band depth studies at more equatorial sites as well as at different latitudes will help determine the relative magnitude of band depth variations expected over the course of a year. Additionally, understanding the importance of latitude on the solar wind hydrogen implantation component of Bennu's 2.7- μm band will strengthen our understanding of solar wind hydrogen implantation on other bodies in near-Earth space.

4.4.4 Data Quality

Comparing multiple datasets, primarily the Baseball Diamond and Final Flyby data, is not without concern as several caveats exist. The EQS3 (12:30 LST) data was selected as the primary station for use by OVIRS as it is the most robust dataset for several reasons. Bennu experienced peak solar illumination during this station and also had lower surface temperatures. OVIRS operated at lower temperatures as well. In comparison, the Baseball Diamond stations, excluding BBD2-refly, observed Bennu when both the asteroid's surface (Figure 4.8) and OVIRS' detector were at higher temperatures, introducing non-linearity at longer wavelengths (see Section 2.3), secondary absorption features (i.e., the 2.99 μm feature seen in Figures 4.3a, 4.5c, & 4.6e), and saturated frames.

The Final Flyby data also suffered from higher surface and detector temperatures, but of perhaps greater impact was the dust coating the detector after the Touch-and-Go (TAG) sample acquisition. The dust reduced radiation transmission by approximately 5% (Lauretta et al. 2022),

which introduces additional uncertainties (Praet et al. 2023). Other aspects of the BBD and BFF bands might also be due to these issues, such as their larger and smaller band widths, respectively, likely explaining the general disuse of these datasets in other studies. However, using data from the entire mission is critical to any temporal study, and presumably many others, which is the most effective method for understanding how solar wind hydrogen implantation delivers OH/H₂O outside of a lab. More detailed calibrations and modelling is required to fully incorporate these datasets into any project. However, as I primarily compared band depths across the stations rather than calculating band-area ratios or conducting a detailed band shape analysis, I still conclude that our work shows a component of Bennu's 2.7- μ m absorption feature is due to solar wind hydrogen implantation.

4.5 Summary & Conclusions

I analyzed the 2-4- μ m spectral region on the near-Earth asteroid (101955) Bennu in order to assess its 2.7- μ m absorption feature for temporal variations. This feature, indicative of O-H bonds, is globally present on Bennu with depths of 12-17% due to magnesium-bearing native phyllosilicates (Simon et al. 2020b; Simon et al. 2020a). Nominally anhydrous bodies have been shown to also possess an absorption feature in this spectral range, though their shallow depths suggest an exogeneous source such as hydrogen implanted by the solar wind, which likely has a temporal component (e.g., Sunshine et al. 2009; Pieters et al. 2009; Clark 2009; De Sanctis et al. 2012; Rivkin et al. 2018; McGraw et al. 2022). I used data at two locations on Bennu from eight flybys/stations during the detailed survey phase of NASA's OSIRIS-REx mission (Lauretta et al. 2017) to look for diurnal and/or annual variations in Bennu's 2.7- μ m band depth and shape that might indicate the band is influenced by solar wind hydrogen implantation.

I compared average spectra from multiple Equatorial Stations for both the mid-latitude

boulder Garuda and the equatorial crater Alicanto and found that the 12:30 LST station (EQS3) produced the deepest band at both sites. The shallowest band was from the 15:00 LST (EQS1) dataset. These diurnal variations strongly suggest that a component of Bennu's 2.7- μm feature is indeed due to hydrogen ions implanted by the solar wind, as the 12:30 LST station received the most incident sunlight and the 15:00 LST station the least. This trend is noticeably opposite that seen on the Moon (Sunshine et al. 2009), the other near-Earth body with a diurnally varying O-H feature, which is likely due to the higher lunar temperatures. Given the similar diurnal variations at both sites on Bennu, it is likely that future studies at other locations on Bennu will yield similar results.

Bennu also appears to experience annual variations in 2.7- μm band depth. The comparisons made at 10:00 LST and 12:30 LST using data from different points in Bennu's orbit (i.e., Baseball Diamonds, Equatorial Stations, and the Bennu Final Flyby) show a complicated relationship between heliocentric distance, Bennu's orientation relative to the Sun, and band depth. The incorporation of data rarely used due to its temperature-related uncertainties likely obscures these relationships as well. However, most of the annual variations can still be linked to more or less exposure to solar wind particles. Conducting annual temporal analyses at more sites on Bennu, as well as on other objects for which 2-4- μm data has been collected, should clarify the relationship between solar orientation and band depth. The strong diurnal and weaker annual trends in band depth show that solar wind hydrogen implantation acts on nominally hydrated bodies like it does on nominally anhydrous bodies, thereby verifying the ubiquity of solar wind hydrogen implantation on bodies in near-Earth space.

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5. Conclusions & Future Work

In this dissertation I use near-infrared (NIR) spectroscopy to remotely characterize OH/H₂O on near Earth asteroids (NEAs). By analyzing the 2-4- μ m spectral region, I have greatly increased our overall understanding of OH/H₂O in near-Earth space, including its sources and delivery mechanisms. In Chapters 1 and 2, I show that ground-based observations are suitable for finding OH/H₂O signatures and that nominally anhydrous NEAs often have OH/H₂O. In Chapter 3, I show that a single planetary body can possess OH/H₂O from multiple sources.

In Chapters 1 and 2, I identify the factors that control OH/H₂O delivery and/or retention. In Chapter 1, I present spectra of 29 NEAs and 2 Main Belt Asteroids (MBAs) that show exogenous OH/H₂O is common on S-complex asteroids with aphelia such that they enter the Main Belt. I show four band shape types that result from different OH/H₂O sources and compositions. The wide and narrow linear band shape types result from solar wind hydrogen implantation and are caused by primarily OH. The wide bowl-like band shape type indicates the presence of H₂O that was likely delivered by a carbonaceous or cometary impactor. The final band shape type, a narrow bowl, is the most common and suggests a mix of OH and H₂O is present and was altered by a secondary process like recombinative desorption after hydrogen ions were delivered by the solar wind. In Chapter 2, I further test these results on three specific NEAs and find a spatial dependence for band depth and/or shape regardless of OH/H₂O delivery mechanism.

In Chapter 3, I show that hydrated bodies can also have OH/H₂O that is delivered via solar wind hydrogen implantation. I analyze data from the OSIRIS-REx mission to show that (101955) Bennu's deep hydration feature varies temporally. These temporal variations are most

easily explained as the solar wind creating OH/H₂O by implanting hydrogen ions. Results from these studies all show that OH/H₂O is ubiquitous in near-Earth space and that the processes that create it are ongoing.

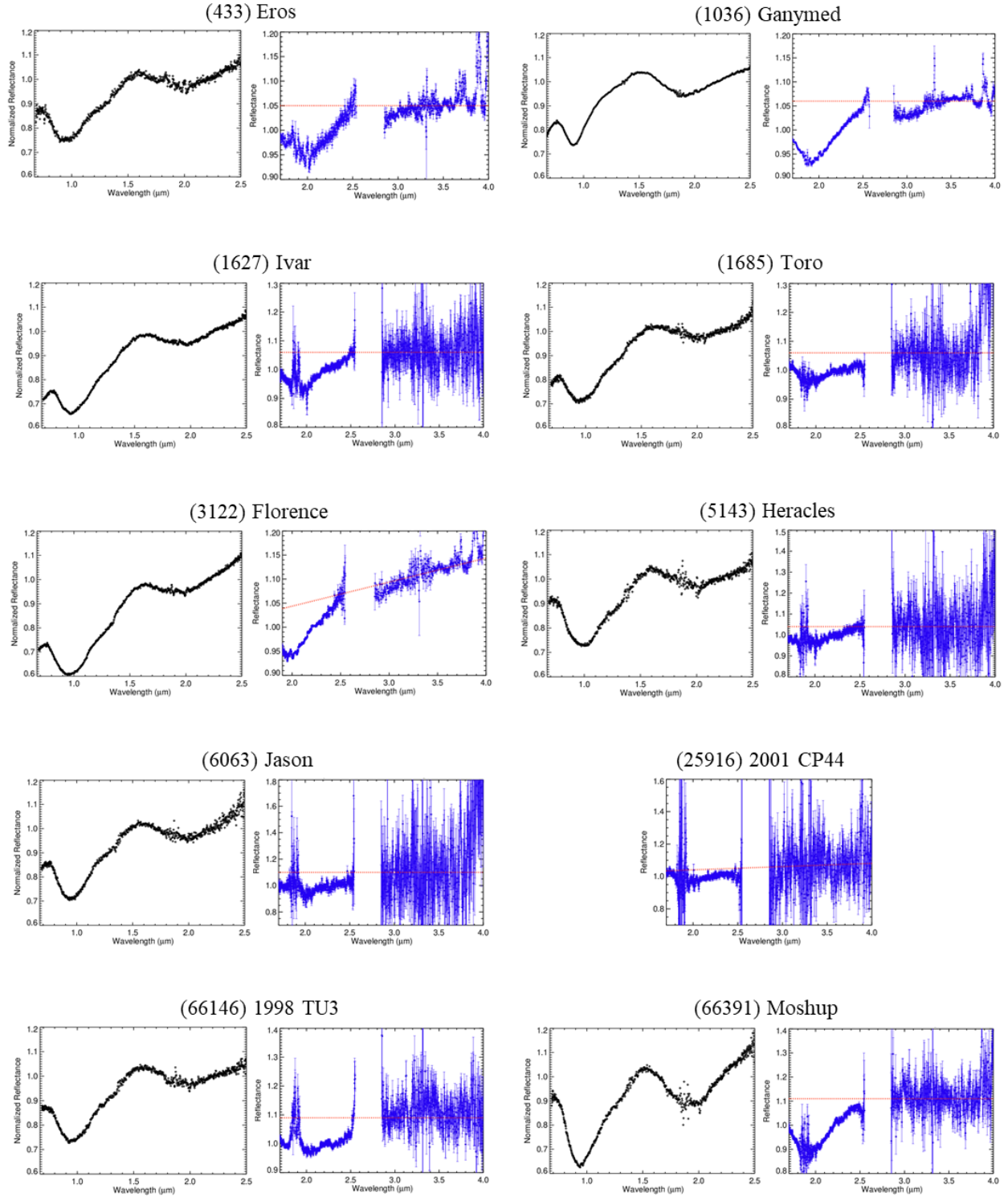
While ground-based observations will continue to be the primary mode of furthering the characterization of OH/H₂O in near-Earth space, future work utilizing alternative methods will help verify the predictions made in the above-detailed studies as well as increase the useability of the 3- μ m band for compositional determinations. The inability to study the entire hydration band using ground-based telescopes severely hinders band analysis and the assessment of hydrated material composition and source. A space-based observatory, such as NASA's James Webb Space Telescope (JWST), is ideally suited for studying hydration features. JWST can collect data across the entire 2-4- μ m spectral region, which would allow the band center or minimum to be determined in addition to characterizing the shape of the full hydration feature. Such a study could be used to test the band shapes described in Section 2 as well as further probe the causes of the band depth variations discussed in Section 3. Additionally, the Mid-Infrared Instrument (MIRI) on JWST can collect data between 5 μ m and 28 μ m. This added spectral coverage allows for more detailed analysis on the silicates present and how they affect OH/H₂O delivery and/or retention (see Section 3.5.1), as well as offering a definitive method of determining the presence of H₂O. Water has a bending mode that correlates to an absorption feature around 6 μ m, so this spectral region can be used to distinguish between OH and H₂O, which is more difficult when only considering the 2-4- μ m range.

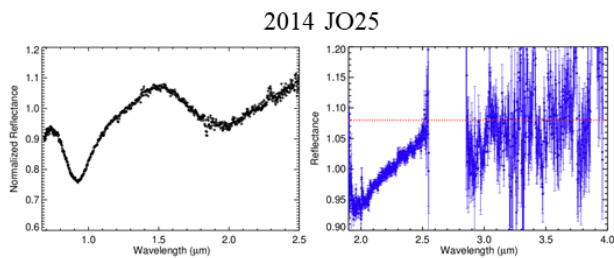
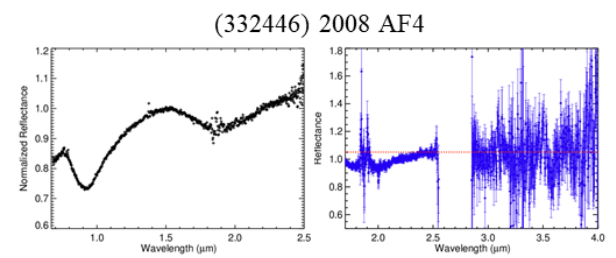
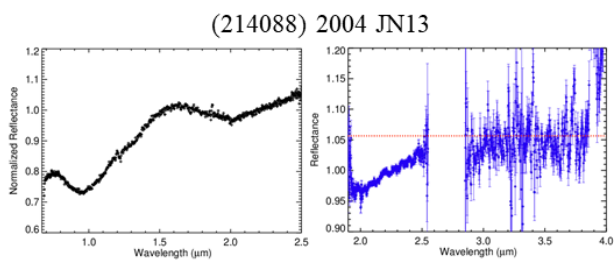
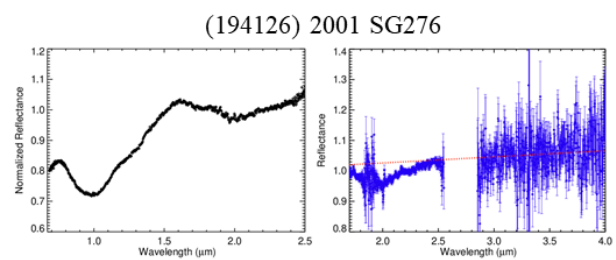
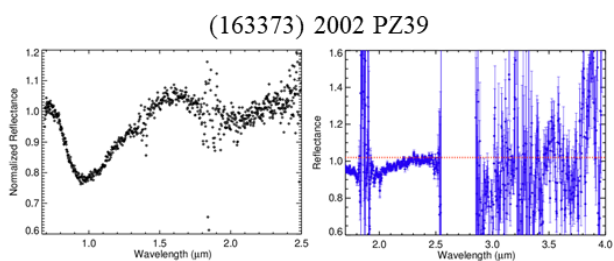
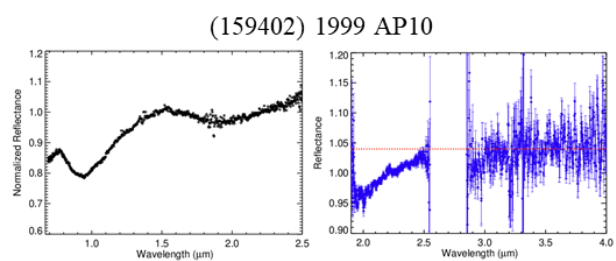
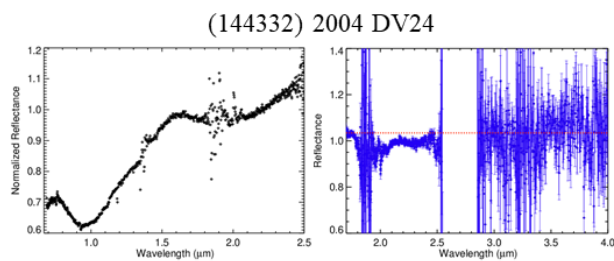
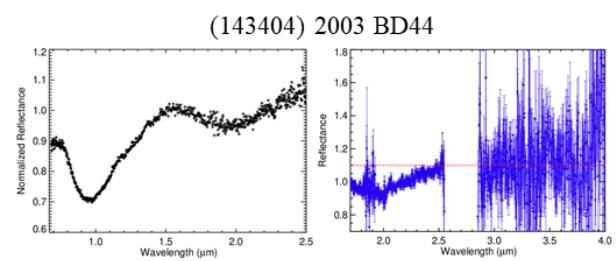
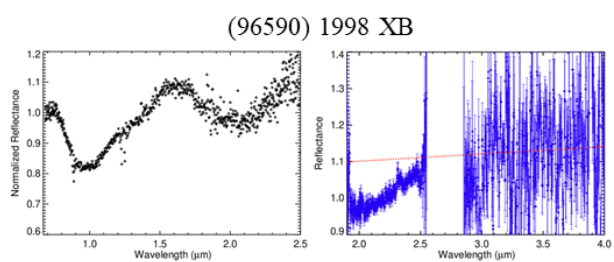
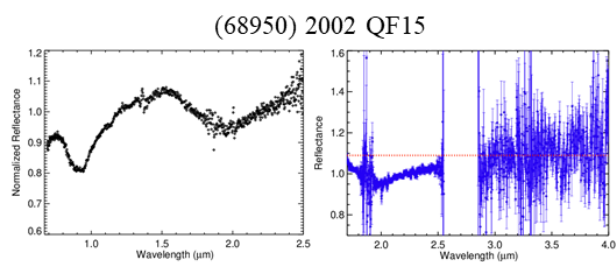
Lab work in addition to a space-based study would further constrain the 3- μ m hydration feature such that it could be used to make analyses of a similar style to those made using the 1- and 2- μ m bands. Synthesizing absorption features in the lab that match those observed by JWST

and the IRTF could help determine the exact species and quantity of OH/H₂O required to make each feature. Other lab projects, such as determining which mixtures of carbonaceous and pyroxene-rich materials produce a Vesta-like band, would also aid in quantitatively studying the 3- μ m feature in a manner not feasible when using only ground-based observations. Combining lab work and space-based observations with the ground-based observations presented in this work, as well as future ground-based observations, will build on the predictions made herein and increase the general understanding of the mechanisms by which OH/H₂O is delivered to objects in near-Earth space.

Appendix A

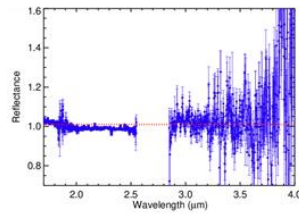
S-Complex Spectra





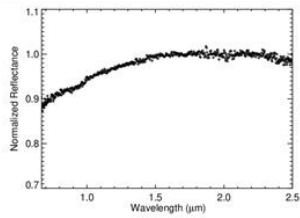
C-Complex Spectra

(3200) Phaethon

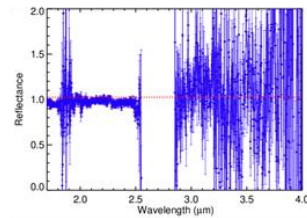


X-Complex Spectra

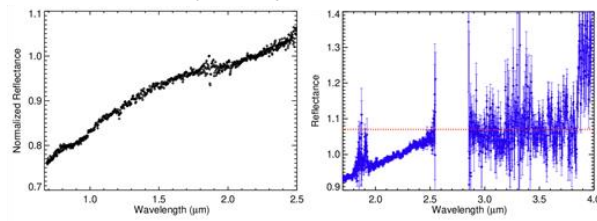
(54789) 2001 MZ7



(85275) 1994 LY

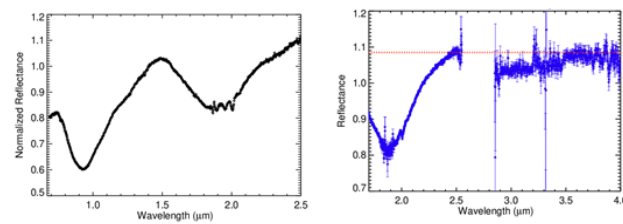


(153201) 2000 WO107



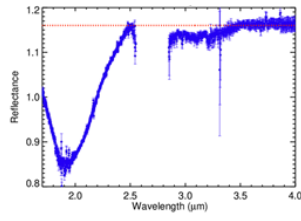
R-Type Spectra

(349) Dembowska

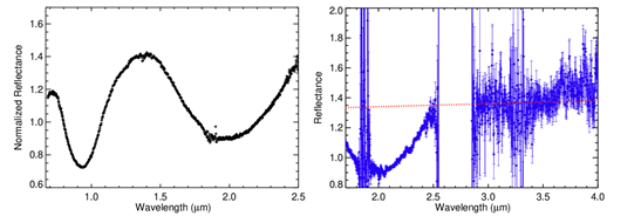


V-Type Spectra

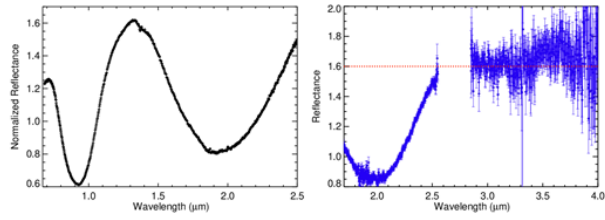
(4) Vesta



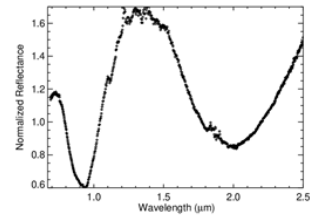
(1981) Midas



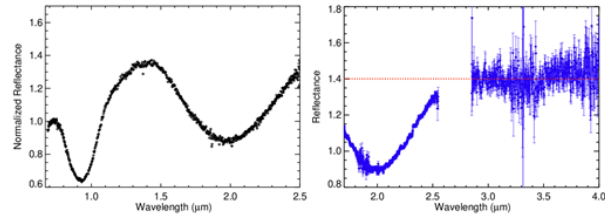
(163696) 2003 EB50



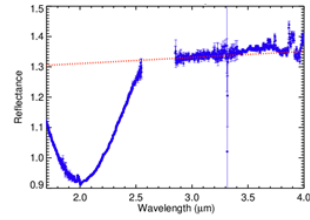
(164121) 2003 YT1



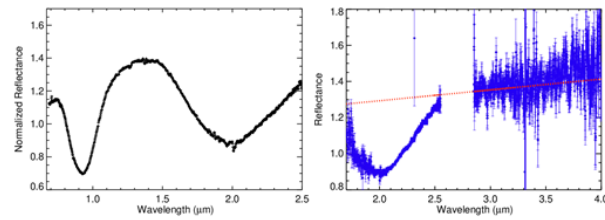
(285944) 2001 RZ11



(357439) 2004 BL86



(454177) 2013 GJ35



Appendix B

Table B.1: Frames used for Garuda Temporal Analyses

Station	ID	SCLK	Bore Latitude (°)	Bore Longitude (°)
BBD3	326027	606462566	-38.70	263.57
	326142	606462682	-38.73	260.90
	326143	606462683	-37.83	260.88
EQS1	357551	609495750	-38.06	265.56
	357715	609495900	-38.27	262.00
	357809	609495986	-37.20	260.05
EQS3	407293	610700072	-38.19	265.70
	407388	610700159	-38.94	263.76
	407550	610700308	-37.78	260.17
EQS4	450213	611301561	-39.33	262.22
	450296	611301649	-38.25	260.14
	465197	611317036	-37.52	262.16
	465266	611317122	-38.89	260.30
BFF	803627	671039469	-40.01	264.40
	803628	671039470	-38.49	264.16
	837836	671054699	-38.36	265.75
	837946	671054800	-39.33	263.34
	837947	671054801	-37.81	263.45
	838147	671054984	-38.24	258.92

Table B.2: Frames used for Alicanto Temporal Analyses

Station	ID	SCLK	Bore Latitude (°)	Bore Longitude (°)	Station	ID	SCLK	Bore Latitude (°)	Bore Longitude (°)
BBD1	289767	605264945	5.68	108.30	EQS5	486311	611925422	2.59	112.84
	289768	605264946	4.37	109.32		486312	611925423	0.24	112.73
	289769	605264947	2.86	110.49		486313	611925424	-2.14	112.89
	289770	605264948	1.45	111.59		486314	611925426	-4.77	113.31
	289771	605264949	0.02	112.70		486396	611925526	-4.81	111.15
	289772	605264950	-1.45	113.84		486397	611925527	-2.33	110.61
	289773	605264951	-2.94	115.01		486398	611925528	0.09	110.22
	290002	605265160	5.86	110.42		486399	611925530	2.65	110.26
	290003	605265161	4.43	110.34		486400	611925531	5.04	110.02
	290004	605265162	2.93	110.24		485487	611925647	2.80	106.83
	290005	605265163	1.37	110.14		485488	611925648	0.52	106.56
	290006	605265164	-0.21	110.04		485489	611925649	-1.88	107.05
	290007	605265165	-2.01	109.93		485490	611925650	-4.62	107.98
	290008	605265166	-3.68	109.83		555820	622797324	5.16	112.64
	290009	605265167	-5.35	109.73		555821	622797325	2.83	112.66
BBD3	332912	606469072	4.92	112.14	BBD2- refly	555822	622797327	0.20	112.65
	332913	606469073	3.61	112.12		555823	622797329	-2.39	112.68
	332914	606469074	2.29	112.11		555824	622797331	-4.94	112.72
	333003	606469075	0.83	112.10		555937	622797538	-5.64	108.00
	332915	606469076	-0.48	112.09		555938	622797540	-4.78	107.91
	332916	606469077	-1.79	112.07		555939	622797542	-4.12	107.83
	332917	606469078	-3.11	112.05		555940	622797543	-3.60	107.77
	333004	606469079	-4.43	112.03		555941	622797545	-3.23	107.70
	332918	606469080	-5.76	112.01		555942	622797547	-2.97	107.63
	333108	606469242	-5.45	108.29		555943	622797549	-2.86	107.58
	333109	606469243	-4.13	108.28		555944	622797551	-2.86	107.54
	333110	606469244	-2.82	108.26		555945	622797553	-2.84	107.49
	333111	606469245	-1.52	108.24		555946	622797554	-2.82	107.44
	333112	606469246	-0.23	108.22		555947	622797556	-2.80	107.39
	333113	606469246	1.04	108.20		555948	622797558	-2.79	107.34
	333114	606469247	2.46	108.16		555949	622797560	-2.78	107.29
EQS1	333115	606469248	3.75	108.13		555950	622797562	-2.76	107.25
	333116	606469249	5.04	108.11		555951	622797564	-2.75	107.19
	347811	609486828	-2.82	113.46		555952	622797565	-2.74	107.15
	347812	609486829	-1.00	113.43		555953	622797567	-2.73	107.11
	347813	609486830	0.82	113.41		555954	622797569	-2.71	107.06
	347814	609486831	2.67	113.38		555955	622797571	-2.69	107.02
	347936	609486944	4.20	110.65		562925	622797573	-2.67	106.97
	347937	609486945	2.37	110.63		555956	622797575	-2.65	106.93
	347938	609486946	0.54	110.61		555957	622797576	-2.64	106.88
	347939	609486946	-1.26	110.60		562926	622797578	-2.62	106.84
	347940	609486947	-3.06	110.58		555958	622797580	-2.60	106.80
	348020	609486948	-5.08	110.57		555959	622797582	-2.57	106.76
	348066	609487062	-3.77	108.02		555960	622797584	-2.55	106.71
	348067	609487063	-1.73	108.00		555961	622797586	-2.53	106.67
	348068	609487064	0.07	107.98		555962	622797587	-2.52	106.62
	348069	609487065	1.88	107.95		555963	622797589	-2.50	106.58

	348070	609487066	3.73	107.93		562927	622797591	-2.48	106.54
	414362	610706547	-2.84	114.20		555964	622797593	-2.46	106.49
	414363	610706548	-1.06	114.19		562928	622797595	-2.44	106.44
	414364	610706549	0.72	114.19		562929	622797596	-2.42	106.40
	414365	610706550	2.50	114.18		555965	622797598	-2.40	106.36
	414494	610706668	4.82	111.37		562930	622797600	-2.38	106.32
	414495	610706669	3.05	111.34		562931	622797602	-2.36	106.27
	414496	610706670	1.28	111.30		562932	622797604	-2.34	106.22
	414497	610706671	-0.49	111.27		562933	622797606	-2.32	106.18
	414498	610706672	-2.46	111.23		562934	622797607	-2.30	106.14
	414499	610706673	-4.25	111.20		562935	622797609	-2.28	106.10
EQS3	414500	610706674	-6.05	111.17		819781	671045866	4.78	111.67
	414619	610706783	-5.81	108.69		819782	671045867	3.44	111.79
	414620	610706784	-3.97	108.68		819783	671045868	2.05	111.91
	414621	610706784	-2.15	108.68		819784	671045869	0.69	112.03
	414622	610706785	-0.36	108.67		819785	671045870	-0.64	112.15
	414623	610706786	1.59	108.66		819786	671045871	-1.98	112.27
	414624	610706787	3.36	108.65		819787	671045872	-3.46	112.40
	414625	610706788	5.14	108.65		819788	671045873	-4.79	112.52
	414754	610706906	2.84	105.81		819789	671045874	-6.12	112.64
	414755	610706907	0.92	105.77		819941	671046013	-6.23	109.57
	414756	610706908	-0.81	105.74		819942	671046014	-4.88	109.40
	414757	610706909	-2.59	105.70	BFF	819943	671046015	-3.54	109.24
	456200	611307936	4.14	112.05		819944	671046016	-2.06	109.06
	456201	611307937	1.98	112.12		819945	671046017	-0.74	108.89
	456202	611307938	-0.17	112.18		819946	671046017	0.59	108.72
	456203	611307939	-2.11	112.24		819947	671046018	1.94	108.56
	456312	611308055	-1.69	109.58		819948	671046019	3.32	108.39
	456313	611308056	0.26	109.48		819949	671046020	4.68	108.22
	456314	611308057	2.41	109.36		820093	671046152	1.87	105.39
	456315	611308058	4.58	109.26		820094	671046153	0.39	105.52
	456424	611308174	2.73	106.58		820095	671046154	-0.92	105.63
EQS4	456425	611308175	0.62	106.65		820096	671046155	-2.22	105.75
	456426	611308177	-1.48	106.71		820097	671046156	-3.52	105.86