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Volatile-rich Asteroids in the Inner Solar System

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Abstract

Bennu (101195), target of the Origins, Spectral Interpretation, Resource Identification, Security, Regolith Explorer (OSIRIS-REx) mission, is a type-B asteroid with abundant spectral evidence for hydrated silicates, low thermal inertia "boulders" and frequent bursts of particle emission. We suggest that Bennu's parent body formed in the outer solar system before it was perturbed into the asteroid belt and then evolved into a near-Earth object. We show that this is consistent with models of planetesimal evolution. Bennu has many characteristics expected for a dormant comet, and could potentially contain a minimum of 1 wt.% adsorbed water if its gross mineralogy is consistent with the Orgueil meteorite. This is in addition to any ice or water contained within the hydrous minerals themselves. Based on this hypothesis, we predict the properties of the samples that will be returned to Earth by the OSIRIS-REx mission, including abundant phyllosilicate minerals, amorphous hydrated silicates and low-density, very high-porosity aggregates, already observed by the OSIRIS-REx instrument suite. We predict enrichments in D/H and $^{15}N/^{14}N$, high C/Mg ratios (>~7 wt%), and a greater range of organic compositions than found in meteorites, including an organic component poor in aromatics, and a more labile organic fraction. Ammonium salts, ranging from NH₄Cl to ammonium-organic acid salts could carry much of the nitrogen in comets, yet only NH₄CH₃COO and heavier salts are sufficiently stable to be found in these returned samples. Water adsorbed onto highly porous grains should also be detected provided that the sample return capsule remains below 300 K during Earth return, and this water should be isotopically heavy.

Unified Astronomy Thesaurus concepts: Near-Earth objects (1092); Meteorites (1038); Main-belt comets (2131)

1. Introduction

The goal of this manuscript is to predict the properties of the sample that will be returned to earth from the asteroid Bennu by the Origins, Spectral Interpretation, Resource Identification, Security, Regolith Explorer (OSIRIS-REx) mission in 2023 September. We hypothesize that Bennu could be a fragment of a dormant comet and begin with a review of the literature to demonstrate that this hypothesis is consistent with previous research on the origins of at least some carbonaceous chondrite meteorites, with dynamic models of the early solar system and with current views on the connections between comets and asteroids. Observations taken by the OSIRIS-REx spacecraft are then briefly reviewed to demonstrate the water-rich nature of Bennu. A calculation of the lower bound on the water content of Bennu is presented based on the hypothesis that it started with a very high water/rock ratio typical of comets and evolved over billions of years to resemble aqueously altered CMs and the Orgueil meteorite, the closest spectral matches to its surface. Our predictions of the physical and chemical properties of the sample are derived from these hypotheses and from direct observations of Bennu.

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Small bodies likely formed in a roughly continuous sequence from dry asteroids near the Sun, through increasingly waterrich bodies near Jupiter and beyond the giant-planet region (Nuth et al. 2018). It is generally assumed that meteorite parent bodies (asteroids) formed inside the orbit of Jupiter, while comets formed outside where very low temperatures promoted condensation of a wide range of volatiles (Dones et al. 2004). As a general rule, comets are thought to be transient visitors to the inner solar system rather than long-term residents. There are at least two accepted mechanisms that can place comets, formed well beyond the Snow Line (Stevenson & Lunine 1988), into long-term residence in the inner solar system (Gomes et al. 2005). One is the evolution of long-period cometary orbits over time while the second is due to giantplanet interactions with the nebular disk early in solar system history.

1.1. Giant Planet-Disk Interactions

Any possible compositional order in the small body population of the early solar system was thoroughly scrambled due to tidal interactions between the growing giant planets and the nebular disk leading to the planets' migration (Gomes et al. 2005; Morbidelli et al. 2005; Tsiganis et al. 2005; Morbidelli & Crida 2007; Walsh et al. 2011; Brasser et al. 2016). Jupiter may have migrated from \sim 3.5 au inward to \sim 1.5 au before reversing direction to end up near its current orbit. Orbits of

the other giant planets evolved in similar fashion. Large-scale migration threw dry bodies into the Sun, into the outer nebula and out of the solar system, while driving water-rich bodies into the inner solar system and into the Sun. Following this chaos, small bodies in the inner solar system formed terrestrial planets, the asteroid belt and the Jupiter Trojans. We note that additional mechanisms have been proposed to deliver water-rich planetesimals from the outer to the inner solar system (Izidoro et al. 2016; Raymond & Izidoro 2017).

1.2. Modern Comets

Comets fall into the inner solar system from the Oort Cloud, the Hills Cloud and the Kuiper Belt via different orbital pathways. Once in the inner solar system their active lifetime is short, (about 1000 perihelion passages) compared with their dynamic stability (Whitman et al. 2006). For typical Jupiter Family Comets (JFC) this leads to an active lifetime on the order of 5000–10,000 yr compared with their dynamic (orbital) lifetime near 500,000 yr. Estimated active lifetimes for long-period comets range from 50 to 2000 perihelion passages (Whitman et al. 2006; Nesvorný et al. 2017) though uncertainties in their dynamic lifetime are much greater. At least for JFCs, the "comet" spends only a tiny fraction of its dynamic lifetime in the active phase and about 98% of its time as an inactive nucleus: 6% of NEOs may be extinct comets (Whitman et al. 2006).

Active asteroids (Hsieh 2017) have been discovered in the main asteroid belt and may represent comets heading toward dormancy after losing most of their surface volatiles. It is difficult, but not impossible, to explain how such objects could transition from a cometary orbit to orbits in the main belt. An alternative is that they were emplaced in the asteroid belt during giant-planet migrations and have slowly evolved to their present state. In contrast, Manx Comets (Stephens et al. 2017) have nuclei with spectral properties of dry, rocky asteroids (SType) yet still display a weak coma such as found in comets and could represent original inner solar system asteroids flung into the Oort Cloud during giant-planet migration that condensed water onto their surfaces prior to their recent deflection into the inner solar system.

1.3. Evidence from Meteorites

Based on eyewitness accounts of its fall, Gounelle et al. (2006) reconstructed the orbit of the CI Orgueil parent body and estimated an atmospheric entry velocity >17.8 m s⁻¹, implying that its aphelion was beyond Jupiter's orbit and therefore that Orgueil was a probable cometary meteorite. Scott et al. (2018) have suggested that CR, CO, and ungrouped Carbonaceous Chondrites (CCs) may have formed beyond Jupiter based on significant isotopic differences between these meteorites and non-CCs. However, unlike Orgueil, there is no evidence that other CCs fell to Earth from cometary orbits. Such primitive chondrites could have formed in the outer solar system, then been emplaced in the inner solar system during the giant-planet migration period and evolved in place since that time.

2. Evolution from Active Comet to Asteroid

If an asteroid class represents an intermediate step from active comet to dormancy, then there are certain observational properties that the class should collectively exhibit. First, as the activity of a comet fades, it is possible that the comet will be observed on one of its last perihelion passages where volatile emission is strong enough to produce an observable coma and/or tail. Subsequent observations could recover the body but not observe cometary features, leading to classification as an asteroid. Later work would show the similarity of the asteroid and cometary orbital elements, leading to realization that the observations are of the same object but at different stages of evolution. Such dual-classed bodies are indeed observed and carry both cometary and asteroid designations.

Some dual-classified objects include comet 107P/(4015) Wilson-Harrington (Fernandez et al. 1997; Ishiguro et al. 2011) and 95P/(2060) Chiron. Both are B-type asteroids, as is the asteroid (3200) Phaethon that is the parent of the Geminid meteor shower and has been observed to be an active source of orbital debris from a comet-like tail. Other dual-class objects include Comet 133P/(7968) Elst–Pizarro (Hsieh et al. 2004, 2009a) a C-type asteroid, 174P/(60558) Echeclus, a D-type Centaur (Jewitt 2015; Wong et al. 2019), and asteroid 176P/(118401) LINEAR (Hsieh et al. 2009b, 2011; de Val-Borro et al. 2012), a B-type "main-belt comet." This list of dual-class objects is far from complete. There is little doubt that many of these objects retain a volatile component that drives the observed particle emissions.

Particle emission events such as those that characterize "main-belt comets" or "active asteroids" are another characteristic of a nearly dormant comet (Hergenrother et al. 2020). However, there are several other mechanisms that might also drive particle emissions. Impacts could drive particles from the surface of a comet or asteroid (Bottke et al. 2020), as could electrostatic lofting (Hartzell et al. 2020), and thermal fatigue (Molaro et al. 2020). Particle emission could be driven by YORP spin up (e.g., Kleyna et al. 2019) or the sudden release of gravitational energy in landslides, all of which could occur at any time throughout the orbit of a small body. Particle emission from a small body spinning very near breakup should also be equally distributed along the orbit.

If we assume that an active comet gradually depletes the volatile content of its near-surface regolith (Fanale & Salvail 1984) or that active regions slowly form an insulating layer of the type studied by Storrs et al. (1988), then volatile-depleted surface layers act as a barrier for both the inward transfer of solar energy as well as for the outward diffusion of water vapor. Water vapor will therefore be adsorbed onto regolith grains for longer timescales than occur in active comets. Longer contact times will allow reactions to cement regolith into coherent "boulders" or layered deposits (Kossacki & Szutowicz 2008) and cementation is powered by the overall reduction in grain surface energy.

Active comets shed tons of particles during perihelion passage that remain in the same orbit as the comet. These debris trails are responsible for meteor streams that produce meteor showers throughout the inner solar system (Jenniskens 2006, Table 9). As a comet evolves toward dormancy, the quantity of debris declines and the density of the meteor stream decreases as the particles diffuse away from the comet's orbit due to their original tangential velocity plus the effects of solar wind and photon pressure. Outbursts from active asteroids can maintain the debris stream after cometary activity ends. Therefore, intense meteor streams associated with an active comet will gradually decay, but may survive at a lower particle density depending on the frequency and intensity of particle

outbursts. Association of a meteor stream with an asteroid is another possible signal that the asteroid is a dormant comet and we note that several B-type asteroids are parents of meteor streams, e.g., 2001 YB5 (Meng et al. 2004), 2005 UD (Ohtsuka et al. 2006) and (3200) Phaethon (Kareta et al. 2018).

The orbit of a comet is not a definitive marker for a volatilerich body formed in the outer solar system. While there are many active comets in "cometary" orbits such as the Jupiter Family or in longer period Halley-type orbits, there should be many more dormant comets in such orbits (Levison & Duncan 1994) as active lifetimes are considerably less than dynamic lifetimes. Therefore, another observable to characterize an asteroid class of dormant comets is that some members of this asteroid type will be members of the Jupiter Family (Carusi & Valsecchi 1987).

To summarize, if an asteroid type represents an evolutionary stage between active and dormant comets, that asteroid type should have some members that fulfill the following criteria. Some will be dual classed. Some will be "active asteroids" with the intensity of activity correlated with solar distance. Some will be parents of meteor streams; and some will occupy "cometary" orbits. Not all class members will fulfill all criteria. However, as they will have evolved from high water/rock ratio bodies toward dormancy by the same general processes as traditional comets, their regolith properties, their spectra and their internal structure and composition should be similar to those of dormant comets evolved in more "comet-like" orbits.

B-type asteroids fulfill all of these criteria. We are not arguing that B-type asteroids represent the only asteroid type derived from active comets. However, as our focus here is Bennu, we are most interested in the relationship between B-type asteroids and comets (e.g., see Cellino et al. 2018). A case can be made that C-type asteroids are also derived from comets while an even better argument can be made for D- and F-types that are more frequently found in JFC and LPC orbits.

3. Physical and Chemical Properties of Dormant Comets

Volatile-poor asteroids that formed with typical concentrations of radiogenic elements evolve as metamorphic systems forming crystalline, anhydrous minerals. Asteroids containing higher water/rock ratios may not achieve the high metamorphic temperatures of "dry" asteroids if the water evaporates from the body, carrying off much of this thermal energy. If the water cannot quickly escape, evidence for fluid flow will be observed in elemental depletions, as well as by the deposition of minerals such as carbonates as veins in cracks and voids (Weisberg et al. 2006).

High water/rock ratio bodies are unlikely to have reached temperatures much above the local boiling point of water. First, high water/rock ratios dilute concentrations of radiogenic elements and the potential melting and evaporation of near-surface water carries off a significant fraction of any heat generated by their decay. Second, if water vapor generated by higher temperatures cannot easily escape, then the high internal pressure generated by steam could exceed the local strength of the body forcing open cracks to vent interior heat. The internal composition of a comet will be a mixture of water (and possibly other volatile) ice plus mineral components. The most abundant mineral components are amorphous iron and magnesium silicates (Kolokolova & Jockers 1997; Zolensky et al. 2006) inherited from the interstellar medium, some of which may have been processed by exposure to liquid water

(Chizmadia et al. 2006; Chizmadia 2007; Chizmadia & Lebrón-Rivera 2010; Nakamura-Messenger et al. 2011). This may be mixed with a variety of highly processed anhydrous mineral grains, CAIs, and chondrules transported from the inner solar system (Nuth 1999, 2001; Matzel et al. 2010) depending on the age of the comet (Nuth et al. 2000).

Volatile-rich bodies thrown into the inner solar system that did not fall into the Sun or become incorporated into terrestrial planets had a very wide range of environments in which to evolve, from perihelia near 2 au out to beyond 5 au. Given the dust rich nature of the solar system during the formation of the terrestrial planets (Weidenschilling & Cuzzi 2006), even the innermost planetesimals could have been shielded from direct sunlight for several thousand years, leading to slow and gentle metamorphism of their surfaces. A volatile-rich body driven in to the main asteroid belt by gravitational interactions could evolve over several billion years. It would initially lose nearsurface volatiles to form a coma and tail until such activity is shut down by natural processes (Fanale & Salvail 1984; Storrs et al. 1988). Small impacts could disrupt an insulating crust leading to vaporization of volatiles and the emission of dust until the breach is "healed" by the same triboelectric processes that formed the original insulating layer.

Spacecraft studies of comets 9P/Tempel 1 or 67P/Churyumov-Gerasimenko have enabled detailed models of the evolution of volatiles and regolith that can be directly compared with observations (e.g., Schorghofer 2016). Kossacki & Szutowicz (2008) modeled the loss of water vapor from 9P/Tempel 1 through a dust layer on the surface attempting to match the observed water production rate. In a later study Kossacki et al. (2015) modeled hardening of a granular ice-dust mixture at 67P/Churyumov-Gerasimenko's surface as it evolved with time to produce a hard, meter-thick layer, but only when the dust grains were tens of microns or smaller in radius.

Water-rich bodies emplaced in the asteroid belt would experience much less extreme variations in temperature than JFCs or LPCs, due to their less eccentric orbits. Because of long evolutionary timescales and warmer average temperatures in the inner solar system, we can extrapolate from the models above that slow diffusion of water vapor through regolith could result in thicker monolayer to multilayer regolith deposits than those formed on the shorter timescales above. For regolith layers that had previously lost volatiles via sublimation, reactions of water vapor slowly diffusing through pores could cement such layers into coherent rocks, much like terrestrial sandstones (Boggs 2000). Closer to the Sun, volatiles sublime, leaving behind a residue of insulating silicates (Storrs et al. 1988). Rapid sublimation (e.g., through deep fissures) could carry away mineral matter frozen in ice without producing phyllosilicates. Slow sublimation could empty areas between mineral grains of volatiles while cementing the grains in place at their contact points, resulting in highly porous yet coherent silicate layers. As comets evolve from the active stage toward dormancy, all three processes occur. In addition, not all silicate grains lofted into space leave the comet (Hermalyn et al. 2013). Some porous aggregates fall back to the surface where they adsorb water to become cemented into low-density, layered deposits (Groussin et al. 2015; Thomas et al. 2015; Vincent et al. 2015; Keller et al. 2017).

Main-belt orbits provide long timescales of steady temperatures that maximize production of layered deposits. Impacts break up such layers, reactivating sublimation in some areas. Orbital changes that bring the body closer to the Sun could reactivate much larger areas of crust and result in ejection of large sections of insulating layers or in evaporation of pockets of subsurface ice and collapse of overlying layers into voids (Fulle et al. 2016). Both mechanisms break up large, continuous layers and result in a more jumbled terrain consisting of randomly oriented layered blocks or boulders (Pajola et al. 2015, 2016a, 2016b).

Although many meteorites contain water, the CI carbonaceous chondrites Orgueil and Ivuna show extreme (>10 wt%) hydration (Zolensky & McSween 1988). Based on mineralogical and chemical evidence, including the relatively high D/H ratio of CI chondrites, identical to within uncertainties to Jupiter family comet 103P/Hartley 2 (Hartogh et al. 2011), it was suggested that CI chondrites are fragments of comets or extinct cometary nuclei (Campins & Swindle 1998; Lodders & Osborne 1999). Some meteorites contain significant levels of volatile hydrocarbons as well as water of hydration and salts, such as the ungrouped C2 carbonaceous chondrite Tagish Lake (Brown et al. 2000; Pearson et al. 2006; Alexander et al. 2012, 2013). Gounelle & Zolensky (2014) suggested that these volatile-rich CCs originate from the outer solar system or from comets.

Carbonaceous chondrites (particularly CIs, CMs, and CRs) contain organic material in a variety of forms, both soluble and insoluble, as well as aromatic and aliphatic hydrocarbons (Glavin et al. 2018). In CI and CM chondrites, the bulk matrix is comprised of 2-5 wt% carbon (Pearson et al. 2006; Sandford et al. 2006, 2011). Analysis of CCs revealed a major insoluble organic matter (IOM) component that consists of >50% of the total organic carbon (Alexander et al. 2007). This IOM in chondrites shares a number of similarities with refractory organic material in Chondritic Porous IDPs, which are probably of cometary origin, and with organics emanating directly from comets. Alexander (2011) notes that the bulk composition of IOM normalized to 100 carbon atoms is $C_{100}H_{70-79}N_{3-4}O_{11-21}S_{1-5}$, which is similar to the average composition of Comet Halley CHON particles measured by the PUMA mass spectrometer on Vega 1 (Kissel & Krueger 1987) of C₁₀₀H₈₀N₄O₂₀S₂. Furthermore, both materials share similar enrichments in D/H and $^{15}N/^{14}N$.

Although Sandford et al. (2006) suggested an interstellar or protostellar origin based on these isotopic enrichments, Alexander (2011) notes that such isotopic enrichments are indicative of formation at very cold temperatures and, while favoring a protostellar or interstellar origin, cannot rule out formation in the outer solar system. This carbonaceous material is much more abundant in comets. Based on Mg/C ratios, solar C is \sim 7 wt% in CC IOM but \sim 30 wt% in Comet 1P/Halley CHON particles. Sandford et al. (2011) found that 81P/Wild 2 particles exhibit a greater range of composition, include an organic component poor in aromatics, and contain a more labile fraction. In this sense, cometary organics from active comets seem to be more "primitive" compared with those in meteorites: evolution of this component may include considerable volatile loss, as well as polymerization of the original, cometary organics.

A variety of soluble organic compounds have been found in CI, CM, and CR carbonaceous chondrites including amino acids, carboxylic acids, hydroxy acids, N-heterocycles, polyols, alcohols, aldehydes and ketones, amines, amides, and many

other compound classes (Glavin et al. 2018). In contrast to CM and CR carbonaceous chondrites, which typically contain a complex distribution of amino acids dominated by α -amino acids formed by the Strecker-cvanohydrin synthesis, the CIs Orgueil and Ivuna have a simple amino acid distribution dominated by glycine and β -alanine, an amino acid that cannot be formed by Strecker synthesis (Glavin et al. 2010). These two amino acids could have been synthesized in an early aqueous alteration phase on a parent body that was chemically distinct from the CM and CR chondrites and that was rich in cometary volatiles such as water, ammonia, HCN, and cyanoacetylene (Ehrenfreund et al. 2001). The amino acids glycine and β alanine have also been identified in water extracts of samples returned from Comet 81P/Wild 2 by Stardust, and glycine had a carbon isotopic composition of $\delta^{13}C=+29\pm6\%$ (Elsila et al. 2009) well outside of the terrestrial range and similar to the range of carbon isotopic values that have been measured for glycine in CI and CM chondrites (Ehrenfreund et al. 2001; Pizzarello et al. 2004). Methylamine and ethylamine of cometary origin were also identified in samples returned by Stardust (Glavin et al. 2008). Methylamine and ethylamine are the two most abundant aliphatic amines detected in the CI Orgueil and CM Murchison chondrites, with Orgueil showing a much simpler distribution of amines and a much higher methylamine concentration $(4\times)$ compared with Murchison (Aponte et al. 2015). Volatile glycine accompanied by methylamine and ethylamine were identified in the coma of Comet 67P/Churyumov-Gerasimenko (Altwegg et al. 2016). Altwegg et al. (2016) proposed that glycine may have formed in the ISM or protosolar nebula on dust grain ices.

More recently, Altwegg et al. (2020) reported detection of ammonium salts from a dust grain that collided with the Rosetta spacecraft while it orbited Comet 67P. The grain lodged near the inlet to the ROSINA mass spectrometer and outgassed over many hours. The most abundant component detected was ammonium chloride. Also detected were NH₄CN, NH₄OCN, NH₄HCOO and NH₄CH₃COO. The presence of ammonium salts in or on grains in comets could be a significant source of cometary nitrogen. Although many of these ammonium salts are not stable above 150-200 K (Altwegg et al. 2020), some ammonium salts such as ammonium acetate (NH₄CH₃COO) are stable at or above 300 K and might be returned from Bennu. Analysis of N-containing compounds extracted from the Murchison meteorite found that some NH₃ could have come from ammonium salts or from hydrolysis of extractable organic compounds, although no ammonium salts were directly identified (Pizzarello et al. 1994). Laboratory analyses of the abundance, distribution, and stable isotopic compositions of ammonia, amines, amino acids, stable ammonium salts and other, N-containing organic compounds in samples returned from Bennu and future comet nucleus sample return missions would provide a stronger link between active asteroids, comets, and carbonaceous chondrites.

4. OSIRIS-REx Observations at Bennu

Prior to the launch of the OSIRIS-REx spacecraft, members of the science team assessed Bennu's orbital characteristics and spectrum to derive its most likely pathway to the near-Earth environment. They concluded that Nun (the name that the team gave Bennu's parent body) most likely lived in the inner asteroid belt before it was disrupted via one or more collisions to form Bennu. Collisional disruptions can form linked asteroid

"families." The simulations estimated that Bennu had a 30% chance to be derived from the Eulalia asteroid family and a 70% chance that it was once part of the Polana family (Bottke et al. 2015).

Just prior to arrival at Bennu, the OSIRIS-REx team used the OSIRIS-REx Camera Suite (OCAMS) instrument suite to conduct a careful search for small satellites, dust plumes, and particle emission events (Hergenrother et al. 2019). Orbiting satellites and bursts of particles could pose a hazard to the spacecraft. It was essential to ensure that Bennu's orbital environment was clear of such hazards before the spacecraft entered orbit. No particle emission, dust plumes, or natural satellites were observed during this campaign.

Data obtained by the infrared instruments on approach to Bennu revealed a remarkably water-rich surface with a deep absorption feature at 2.7 microns as recorded by the OSIRIS-REx Visible and Infrared Spectrometer (OVIRS; Hamilton et al. 2019). The water-rich character of Bennu was also evident in longer wavelength spectra by the OSIRIS-REx Thermal Emission Spectrometer (OTES; Hamilton et al. 2019) where the global spectrum of Bennu most closely resembles that of the CI carbonaceous chondrite Orgueil and aqueously altered CMs. The spectrum of Bennu is remarkably uniform (to within a few percent) on spatial scales of tens of meters over the surface of the asteroid, consistent with hydration on large scales. The crater size-frequency distribution suggests that the surface is much older than previously expected (Walsh et al. 2019) with a surface age between 100 million and one billion years. Space weathering on these timescales could contribute to large-scale spectral homogeneity. The surface is covered in large boulders, but these have very low thermal inertia and could therefore be extremely porous (DellaGiustina et al. 2019). The boulders themselves have a blocky, layered texture (Jawin et al. 2020), show evidence for large cracks and may have a matrix that is easily eroded by thermal stresses (Molaro et al. 2020) and solar wind exposure (DellaGiustina et al. 2019; Walsh et al. 2019).

Observations of particle emission were first detected near perihelion at \sim 0.9 au during the first week of the "Orbital A" mapping campaign, prior to which the OSIRIS-REx cameras were less likely to have seen such particles (Lauretta et al. 2019). The project made changes to allow searches for new particle emission events and previous images were examined to check for prior events. The largest particles detected are on the order of 3-7 cm in diameter depending on their albedo. The earliest confirmed particle was detected on 2018 December 10 (∼1 month before perihelion). Bennu's observed particle emission events occurred both on the sunlit side of the asteroid as well as on the dark side (Lauretta et al. 2019). Some particles were observed to be in orbits around Bennu (Chesley et al. 2020) that could be followed for up to several days. While the majority of ejected particles re-impact the surface and may explain the large number of small rocks sitting on the tops of the many large boulders (Rizk et al. 2019), \sim 15% escape (Chesley et al. 2020). Particle monitoring has shown that emission occurs all along Bennu's orbit, including near aphelion (Hergenrother et al. 2020). Data have not yet been corrected for observing geometry, spacecraft distance to Bennu, the intermittent nature of the observing campaign or other factors effecting particle detection efficiency. It is not yet possible to correlate the number of ejected particles and rates of particle emission with solar distance.

Bennu is a type-B asteroid and the observed particle emissions are consistent with a volatile-driven process (Hsieh et al. 2004). Other mechanisms have been suggested to explain these emissions (Lauretta et al. 2019) and may play a role (or even dominate) at specific times throughout Bennu's orbit. While Bennu's weak particle emissions could not have been viewed from Earth, the largest particle emission events have occurred near perihelion as do emissions from other active asteroids. If these emission events are driven by volatiles, then this weak activity level indicates that Bennu has likely lost a large fraction of its initial volatile content compared with these other bodies and is therefore likely to be older. This is consistent with its derived crater age of ~500 million years (Walsh et al. 2019). Observations of particle emission events that originated on the dark side of Bennu suggest that there may be transient pockets of water beneath Bennu's regolith.

Rivkin et al. (2015) point out that three members of the Themis dynamical family are active asteroids (133P, 176P, and 288P) and that transient water ice was observed on the surface of Themis (Campins et al. 2010; Rivkin & Emery 2010) suggesting a reservoir within the body. Therefore at least some members of the Themis family in the Main Asteroid Belt still contain significant water reservoirs despite extensive collisional disruption. This could also be true for members of the Polana and Eulalia families. We note that (142) Polana is a B-type asteroid (Walsh et al. 2013). The surface of Bennu is extensively hydrated and must once have had a much higher water/rock ratio than at present. Where is Bennu's water?

5. How Much Water Could Still Be Contained within Bennu?

One can make an estimate of the current potential water content of Bennu based on thermal modeling and the properties of the regolith observed to date. Rozitis et al. (2020) used a 75 cm Bennu global shape model combined with the Advanced Thermophysical Model to compute temperatures over Bennu's surface and interior. They find that ice could be stable over geologic timescales at several meter depths at Bennu's poles, but not at lower latitudes. In a similar calculation Schorghofer (2008) found that shallow ice deposits could be stable over the age of the solar system in the Main Asteroid Belt. This could potentially explain the activity of active asteroids and observation of surface ice for members of the Themis family. However, ice is not the only potential source of water on Bennu. Significant quantities of water must be bound within phyllosilicates or amorphous hydrated silicates. Another, more mobile source of water is vapor adsorbed on grain surfaces throughout the interior.

We will use the Orgueil meteorite as a proxy for the grain size distribution within Bennu. MacKinnon & Kaser (1988) found that the root mean square grain size distribution within Orgueil matrix peaked at between 50 and 75 nm. This is a much narrower distribution than measured for the more highly evolved matrix of the Alais meteorite. Buseck & Hua (1993) report that phyllosilicates in Orgueil can be smaller than five nanometers in diameter. For a lower limit estimate, we will assume a homogeneous matrix grain size, 50 nm in diameter, throughout Bennu's interior and we will assume that half of Bennu's mass consists of matrix, even though matrix comprises a much larger fraction (up to 99%) of CI meteorites. We calculate the total number of grains and their total surface area assuming they are spherical and that they have the same density

as montmorillonite (2350 kg m⁻³). We note that irregular shaped grains have a greater surface area per unit mass than similar-sized spherical grains and that amorphous hydrated silicates will be less dense than more ordered phyllosilicate minerals of similar composition. Finally, we assume that each grain is covered by a single monolayer of water rather than multiple layers that are feasible for defect-laden amorphous silicates. These assumptions should produce a significant underestimate for Bennu's adsorbed water content.

Bennu's mass is 7.329×10^{10} kg (Lauretta et al. 2019). If half of that mass $(3.6645 \times 10^{10} \text{ kg})$ is in 50 nm diameter grains of density 2350 kg m^{-3} there are $\sim 3 \times 10^{29}$ particles, each with a surface area of $\sim 8 \times 10^{-15}$ m² for a total surface area of $\sim 2.4 \times 10^{15}$ m². On a flat surface, there are $\sim 10^{19}$ water molecules per square meter (more can fit onto curved surfaces), or about 2.4×10^{34} water molecules adsorbed onto the grains within Bennu. This is $\sim 4 \times 10^{10}$ moles of water or about 7×10^8 kg. We note that this estimate is not very sensitive to the assumed grain size: for a given mass, a smaller radius increases the total number of grains, while the surface area of each grain decreases. For a fixed grain mass, the total surface area is proportional to (grain radius) $^{2/3}$. Based on our most conservative estimate for the fraction of water adsorbed within Bennu, we find a water content of \sim 1% by mass. A much less pessimistic calculation based on dehydration of a higher water/rock ratio parent body (e.g., >90% of Bennu's interior mass is matrix << 50 nm in diameter and each irregularly shaped, amorphous grain is less dense than montmorillonite and covered in multiple layers of water) could increase the potential mass of adsorbed water to as much as \sim 5%–10% of Bennu's mass.

This simple calculation shows that Bennu could contain as little as 1 wt.% to as much as ~10 wt.% adsorbed water in addition to ice deposits at the poles or the internal water in hydrated amorphous silicates. It seems likely that the exterior of Bennu (exposed to space) contains a smaller fraction of adsorbed water than the interior. This concentration gradient would drive continuous migration of water vapor toward the surface where it could be concentrated within voids. Slow diffusion of water vapor from the interior to the surface could power low levels of particle emission. As the vapor originates in the deep interior, the flow would be greatest through voids and cracks leading to the surface and may not be directly correlated with surface temperatures. Slow diffusion would be analogous to a distillation process that has continued for millions of years and that should result in preferential loss of lighter water isotopes.

6. Some Predicted Properties of Bennu Samples

There are some predictions concerning the properties expected of the returned samples that are easily derived from the data obtained to date by OSIRIS-REx. First, samples will contain copious quantities of phyllosilicates or amorphous hydrated silicates. Both OVIRS and OTES (Hamilton et al. 2019) demonstrated the presence of hydrated silicates uniformly distributed over Bennu's surface. Data from both spectrometers confirmed the global nature of hydration and the team has only noted slight variation (e.g., $\sim 5\%$) in relative intensity of these spectral features. Therefore predicting that Bennu samples will contain a component similar to the composition of the Orgueil meteorite and aqueously altered CMs is well supported by in situ observations.

Observations by OCAMS clearly show the presence of brecciated boulders, with more durable, higher-albedo clasts eroded from a darker matrix (Pajola et al. 2020). While current observations show the presence of meter-scale clasts (Jawin et al. 2020), there is no reason to suspect that the size distribution does not extend to much smaller scales. Smaller, higher-albedo rocks distributed across the surface are consistent with pyroxene (DellaGiustina et al. 2020). These could be debris accumulated over the 100-1000 million years that the surface has been exposed, while the clasts within larger boulders might represent accumulation of debris by the parent body, Nun, which was "baked-in" to layered deposits as these were dehydrated. Similarly, collisional breakup of Nun would provide more opportunities to cement meteoritic debris into amorphous, hydrated silicate layers forming on newly exposed surfaces.

We hypothesize above that thick surface layers formed by slow diffusion of water vapor from the interior. If we assume a relatively uniform water/rock ratio appropriate for an object formed in the outer solar system (about 3:1), assume that ice is present as well-mixed, small solid particles, then as these particles sublime, and volatiles diffuse outward, they will leave voids. Radiation damaged silicates, primitive amorphous silicates and even crystalline silicates that touch one another at "points" react (aided by surface free energy) with water vapor to form amorphous hydrated silicates (Nakamura-Messenger et al. 2011). These new connections cement particles together. The resulting crust will be an extremely porous yet coherent structure of very low density and low thermal inertia. It could display layers of several successive episodes of water loss and these layers will break into blocky chunks when Nun is disrupted.

Bennu's bulk density as measured by the OSIRIS-REx team is 1190 kg m⁻³. If Nun initially had a lower bulk density more typical of comets then increased density could be accounted for due to both loss of ice and gravitational settling of Bennu's non-volatile components following the breakup of Nun. Bennu is a rubble pile (Barnouin et al. 2019; DellaGiustina et al. 2019) and was thus reassembled after at least one major collision that shattered its parent body. Energy in the collision would lead to evaporation of some internal ice. Exposure of smaller icy fragments, especially if a collision occurred in the inner solar system, would lead to additional evaporative loss of ice. Preferential ice loss (1 g/cc) compared with mineral matter $(\sim 2.5 \text{ g/cc})$ naturally leads to a higher density secondary body. Re-accretion of collision fragments leads to a mixture of boulders and voids that settle into a denser body over time. The observed combination of interior heterogeneity and Bennu's top shape indicate past, spin-induced failure that is consistent with gravitational settling (Scheeres et al. 2019).

The current surface of Bennu may be older than 500 million years. Layers of cemented silicates and other debris may have been exposed to impacts, YORP spin up, gravitational settling over voids and other processes that break larger layers into smaller pieces. Space weathering also appears capable of excavating harder clasts from softer matrix, leading to loss of interior voids in the crust and formation of denser regolith. This model is consistent with observation that thermal inertia is lowest in the largest boulders and increases as these are broken down and compacted due to impacts or the decay of void structure due to fragmentation or space weathering. For the centimeter scale samples that OSIRIS-REx will return, we

predict that some highly porous aggregates will fragment during the collection process, but that porous submillimeter fragments will survive along with more coherent pebbles in the breccia and denser matrix grains.

Observation of volatile-driven particle ejection events indicates that there might be a significant source of water deep inside Bennu that acts as a reservoir for volatiles. Water steadily diffuses to the surface driven by the inward flow of thermal energy. Bennu regolith samples should contain some level of adsorbed water within the microporous silicate matrix. While some adsorbed water may be lost during transport, especially if the TAGSAM reaches its maximum allowable temperature and if individual aggregates are fragmented during collection. However, the largest matrix fragments may still contain measurable quantities of adsorbed water and this water should be enriched in D, ¹⁷O and ¹⁸O.

Deeper levels of these porous silicate layers could be sufficiently warm and could accumulate enough water vapor within pores to produce liquid water. In the presence of primitive organic materials, exposure to liquid water could form a range of organic acids and deposits of carbonates or other mineral species within pores. It may be possible that at least some of the bright clasts observed within the dark rock matrix of the large boulders on Bennu's surface are carbonate deposits precipitated from an aqueous fluid. The distribution of minerals and soluble organic compounds in samples returned from Bennu will help constrain the degree of alteration and potential links to CI and CM carbonaceous chondrites while the ages of such precipitates could potentially show evidence for recent aqueous activity.

The organic composition of samples returned from Bennu should be intermediate between the organics found in primitive carbonaceous chondrites and the organics observed in active comets. They should have enrichments in D/H and $^{15}N/^{14}N$, high C/Mg ratios ($>\sim$ 7 wt%) and exhibit a greater range of compositions than found in meteorites, including an organic component poor in aromatics relative to aliphatics, and a more labile organic fraction. If Bennu is CI-like, returned samples should have a relatively simple amino acid distribution of amines and amino acids dominated by methylamine, glycine, and β -alanine. Overall, Bennu's organics should represent a more primitive distribution of compounds than found in carbonaceous chondrites, and, given the mineralogical evidence for extensive aqueous activity (Kaplan et al. 2020), a more evolved suite of soluble organic compounds than found in primitive carbonaceous chondrites and future samples returned from active comets that did not experience significant aqueous alteration.

Finally, if the TAGSAM temperature remains below 300 K, we may expect to detect NH_3 derived from ammonium salts such as ammonium acetate (NH_4CH_3COO). It is possible that additional, less volatile organic salts could also be detected. Because these salts could be a major carrier of nitrogen in 67P/Churyumov-Gerasimenko, analysis of these materials would be essential in the determination of the bulk $^{15}N/^{14}N$ ratio in Bennu.

7. Conclusions

The active stages of comets represent a relatively short span of their dynamic lifetime. Water-rich planetesimals formed in the outer solar system could have been deflected into the inner solar system during giant-planet migration. These planetesimals would then evolve slowly in the main asteroid belt over the next 4 billion years. We argue that type-B asteroids as a class fulfill all of the criteria expected for an asteroid class that represents the transition from a water-rich to a water-poor body. Bennu is a type-B asteroid and we hypothesize that it was once water-rich. Bennu's dynamic evolution indicates an origin from a parent body in the main asteroid belt. We hypothesize that Nun was emplaced in the main belt as the result of gravitational scattering in the early solar system due to interactions between growing giant planets and the nebular disk. It then evolved chemically and dynamically over the next four billion years. A less probable alternative is that Bennu's parent body was a classic active comet that evolved to become part of the main belt or NEO population as it lost most of its volatiles.

Bennu's surface, is consistent with an extremely hydrated mineralogy. Many boulders are low-density, high-porosity aggregates consistent with formation by slow desiccation of a high water/rock agglomerate at the surface of a comet. Slow desiccation is also consistent with the uniformly hydrated mineralogy of Bennu's surface. Bennu's particle emission could be caused by a number of processes (Lauretta et al. 2019) including volatile-driven emission, a thermal mechanism that would be consistent with observations of other type-B active asteroids.

If Bennu is a fragment of a dormant comet then returned samples could contain adsorbed water as well as water of hydration, provided that TAGSAM does not get warm enough to completely dehydrate the silicates or degas the adsorbed water. Some returned regolith should consist of aggregates of fine, low-density particulates cemented at contact points by hydrous, amorphous silicates and/or organic materials formed under aqueous conditions. The organics should be more primitive (less aromatic, more labile) than those found in carbonaceous chondrites, should be enriched in D/H and $^{15}\mathrm{N}/^{14}\mathrm{N}$ with a simple distribution of amines and amino acids that may be dominated by methylamine, glycine, and β -alanine. We also predict the presence of a suite of moderately volatile ammonium salts bound to halogens and organic acids that could contain a significant fraction of the nitrogen returned from Bennu.

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