Flying too close to the Sun – *the viability of perihelion-induced aqueous alteration on periodic comets*

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Abstract

Comets are typically considered to be pristine remnants of the early solar system. However, by definition they evolve significantly over their lifetimes through evaporation, sublimation, degassing and dust release. This occurs once they enter the inner solar system and are heated by the Sun. Some comets (e.g. 1P/Halley, 9P/Tempel and Hale-Bopp) as well as chondritic porous cosmic dust – released from comets – show evidence of minor aqueous alteration resulting in the formation of phyllosilicates, carbonates or other secondary phases (e.g. Cu-sulphides, amphibole and magnetite). These observations suggest that (at least some) comets experienced limited interaction with liquid water under conditions distinct from the alteration histories of hydrated chondritic asteroids (e.g. the CM and CR chondrites).

This synthesis paper explores the viability of perihelion-induced heating as a mechanism for the generation of highly localised subsurface liquid water and thus mild aqueous alteration in periodic comets. We draw constraints from experimental laboratory studies, numerical modelling, spacecraft observations and microanalysis studies of cometary micrometeorites. Both temperature and pressure conditions necessary for the generation and short-term (hour-long) survival of liquid water are plausible within the immediate subsurface (<0.5m depth) of periodic comets with small perihelia (<1.5 A.U.), low surface permeabilities and favourable rotational states (e.g. high obliquities and/or slow rotational periods). We estimate that solar radiant heating may generate liquid water and perform aqueous alteration reactions in 3-9% of periodic comets. An example of an ideal candidate is 2P/Encke which has a small perihelion (0.33 A.U.), a high obliquity and a short orbital period. This comet should therefore be considered a high priority candidate in future spectroscopic studies of comet surfaces. Small quantities of phyllosilicate generated by aqueous alteration may be important in cementing together grains in the subsurface of older dormant comets, thereby explaining observations of unexpectedly high tensile strength in some bodies.

Most periodic comets which currently pass close to the Sun are dormant, having experienced surface heating, significant cometary activity and dust release in the past. These bodies may be responsible for the partially hydrated cometary micrometeorites we find at the Earth's surface and their aqueous alteration histories may have been produced by perihelion-induced subsurface heating. This is in contrast to radiogenic and impact heating that operated during the early solar system on asteroids. This study has implications for the alteration history of the active asteroid Phaethon, the target of JAXA's DESTINY+ mission.

***Keywords**: Solar radiation; Comets, nucleus; Comets, dust; Comet Tempel-1; Comet Halley*

1. Introduction – laboratory perspective on naturally delivered cometary dust

Chondritic porous (CP) cosmic dust (micrometeorites and interplanetary dust particles [IDPs]) are nominally anhydrous, poorly crystalline silica-rich carbonaceous and porous aggregates composed of nano- to micron-sized grains (Mackinnon and Rietmeijer, 1987; Noguchi et al., 2015; 2017). Their primary components are amorphous GEMS (glass with embedded metal and sulphides [Bradley, 1994; 2019]), which represent either moderately volatile, late-stage nebula condensation products, formed at temperatures <750°C (Keller and Messenger, 2011) or interstellar relict grains, recording formation environments prior to the birth of the solar system at temperatures <200°C (Ishii et al., 2018). Chondritic porous dust also contains crystalline anhydrous silicates, which can vary significantly in solid solution composition within a single particle, spanning the entire range of silicates found within chondrites (Klöck et al., 1989; Flynn, 1994; Noguchi et al., 2017). In addition, more exotic highly refractory Mg-enriched silicates are known, which are otherwise rare or absent among meteorites. They include LIME (low iron Mn-enriched) and LICE (low iron Cr-enriched) silicates (Klöck et al., 1989), kosmochloric (Na-Cr-rich) pyroxenes (*kool grains*, Joswiak et al., 2009) and condensation-crystalized enstatite whiskers (Stodolna et al., 2014). Consequently, the anhydrous silicates within CP-dust are fragments of primitive, high-temperature materials, several of which are associated with condensation crystallization and potentially related to the first-generation chondrules and CAIs.

Chondritic porous dust is closely related to ultracarbonaceous micrometeorites, which contain higher abundances of carbonaceous matter (>50wt.%, Dobrică et al., 2009; Duprat et al., 2010) but are otherwise petrographically similar. Together these two subclasses are widely accepted as cometary in origin, owing to their exotic mineralogies, volatile-rich bulk compositions, unique isotopic signatures – which may show extreme isotopic excursions and distinctive "*bunch-of-grapes*" morphologies (Duprat et al., 2010; Starkey et al., 2014; Noguchi et al., 2015). Likewise, they share many similarities to the known cometary dust recovered from the short-period comet 81P/WILD 2 (Zolensky et al., 2006; 2008; Dobrică et al., 2009). Thus, cometary materials contain high-temperature early-formed refractory silicates intimately mixed with amorphous volatile matrix (GEMS, Fe-oxides and Fe-sulfides) and super-volatiles (carbonaceous matter and ices).

2. Evidence for early stage aqueous alteration in cometary dust

Like all chondritic materials, cometary dust particles preserve a record of its parent body's geological activity. For many of the naturally delivered cometary dust particles evidence for minor or "*early stage*" aqueous alteration has been reported. Several studies describe various stages of hydration and secondary replacement in cometary dust aggregates. This ranges from the leaching of Mg and S and the partial hydration of GEMS (Nakamura et al., 2005; Noguchi et al., 2017; Yabuta et al., 2017) through to their complete conversion to low-crystallinity Fe-rich phyllosilicates and the development of complex multi-species phyllosilicate intergrowths with well-defined lattice parameters (Rietmeijer, 1991). Furthermore, Busemann et al. (2009) identified both carbonates and amphibole (anthophyllite [$Mg_2Mg_5Si_8O_{22}(OH)_2$], occurring in association with GEMS) within a single micrometeorite. This particle purportedly originates from the Pi-Puppid meteor stream (and consequently from the Jupiter family comet [JFC] 26P/Grigg–Skjellerup [Vaubaillon and Colas, 2005]). Both minerals are widely associated with secondary alteration phases in carbonaceous chondrite settings. Amphiboles in particular were a highly unusual discovery, having a hydrated composition (containing structural water) and associated with hydrothermal activity (Dobrică and Brearley, 2014). These phases may represent either alteration minerals or primary condensation phases (although the latter interpretation is

favoured by Busemann et al., 2009). In most instances, aqueous alteration extent in cometary dust is minor, restricted to the hydration of GEMS and their subsequent conversion to Fe-rich proto-phyllosilicates, without the concurrent alteration of mafic silicates (olivine and pyroxene) (Nakamura-Messenger et al., 2011).

Likewise, intense study of the 81P/Wild cometary grains captured and returned by the STARDUST mission has also identified tentative evidence of aqueous alteration. This includes the presence of possible secondary minerals: carbonates (Flynn et al., 2008; 2009), (Ti-free) magnetite (formed by oxidation at temperatures <300°C, Hicks et al., 2017) and Cu-, Zn- and Fe- sulphides (Berger et al., 2011; 2015). Cubanite in particular provides constraints on the comet's alteration environment, limiting conditions between 150-200°C, with alkaline fluids (pH~9) and oxygen fugacities at the iron-wüstite buffer (Berger et al., 2015). However, to date, phyllosilicates have not been observed in laboratory analyses of this comet's mineral assemblage returned by the STARDUST mission (Zolensky et al., 2006; 2008). This is despite the expected survival of phyllosilicate or their decomposition phases within the aerogel capture medium (Noguchi et al., 2007; Zolensky et al., 2008; Wozniakiewicz et al., 2010).

3. Experimental studies constraining the duration of aqueous alteration

Nelson et al., (1987) performed early pioneering aqueous alteration experiments on cometary analogue materials. They used synthetic amorphous magnesio-silica smokes with simple compositions (Mg-SiO) and amorphous structures as approximations of natural cometary dust. These amorphous silicates were reacted with distilled water at several different temperatures (58ºC, 83ºC, 95ºC and 105ºC) under atmospheric pressures (~101kPa) and for durations between 1 and 142 hours resulting in the formation of sepiolite ($Mg_4Si_6O_{15}(OH)_2{\cdot}6H_2O$) – a complex phyllosilicate of the palygorskite–sepiolite group. After terminating each reaction, IR spectroscopy was used to measure the degree of alteration using peak intensity ratios at three key wavelengths, which reflect the decay (11.5µm) of the initial amorphous structure and growth (16µm and 20µm) of hydrated phases. The primary aim was to investigate the kinetics of hydration reactions under conditions relevant to asteroids and comets. This study concluded that reactions occur rapidly (over hours to days) and that reaction rates follow a power law function with a strong temperature dependence (Fig.1). Consequently, over the temperature range (-25ºC to +25 ºC) reaction rates increase five-fold for every +10ºC temperature increase. This translates to reaction half-lives of approximately 80 hours at 80ºC, 300 hours at 50ºC and 2000 hours at 20ºC (Fig.1).

The reactions of Nelson et al., (1987) provide important constraints on the kinetics of hydrated amorphous silicates. However, their experimental products (sepiolite) are more complex partial chain silicates with higher water content than the Fe-rich saponite and serpentines observed in hydrated cometary dust (Noguchi et al., 2017; Yabuta et al., 2017). Thus, although the kinetic temperature dependence relationship measured by Nelson et al., (1987) is likely to be accurate in the general sense (applicable to the hydration of amorphous silicates), the reaction rates and therefore the reaction durations are significant overestimates, since the formation of simpler, less hydrated phyllosilicates requires shorter timescales and possibly lower activation energies. Differences in reaction products between the experiments of Nelson et al., (1987) and the naturally altered materials most likely originate from two sources:

(1) Different starting compositions affect reactions trajectories. Naturally occurring GEMS have stoichiometries of approximately $(Mg,Fe)SiO_3$ (Keller and Messenger, 2011) and thus contain significant Fe^{2+}. In addition, GEMS have embedded metal and sulphide phases with measured bulk S contents at ~2-5 Atomic% (Bradley, 1994). The presence of Fe and S is critical in determining how GEMS alter. This is because first-formed phyllosilicates in cometary dust and chondritic matrix are almost always Fe-rich endmembers, while the Mg in GEMS appears to be more fluid-mobile, being

carried away in the alteration fluid and employed in distal alteration reactions (Leroux et al., 2015; Noguchi et al., 2017).

(2) Additionally, Nelson et al., (1987) used the appearance of 16µm and 20µm peaks in the IR spectrum of their alteration products to confirm the generation of phyllosilicates. However, the IR spectral features of poorly crystalline hydrated silicates will be weak broad and smooth signals and are therefore not easily detected by IR methods. Thus, in the experiments of Nelson et al., (1987) their phyllosilicate detection method is likely to have missed subtle proto-phyllosilicates and instead only registered the formation of well-developed crystalline forms. In this case, the calculated reaction times will be overestimates of the true reaction times needed to form more primitive poorly-crystalline species.

Rietmeijer et al., (2004) built on the experimental design on Nelson et al., (1987), also using amorphous magnesio-silica smokes and investigating reaction products with both IR and TEM (transmission electron microscopy). They similarly concluded that characterisation by IR techniques alone is inconclusive because "fluffy" phyllosilicate forms remain unidentified and that reaction rates determined for the development of sepiolite do not accurately model cometary alteration which produces simpler phyllosilicates. In this study they conclude that sample permeability plays a fundamental role in the rate of alteration. As alteration proceeds porosity decreases dramatically because low-density amorphous structures collapse while hydrated phyllosilicates swell. This behaviour means that further alteration beyond an initial poorly crystalline phase is limited as porosity becomes the rate limiting step.

Later Nakamura-Messenger et al., (2011) performed aqueous alteration experiments using pre-characterised anhydrous CP-IDPs as the starting material. They exposed these natural samples to neutral and alkaline water (pH 7-13) at temperatures between 25°C and 160°C for durations between 12-48 hrs. These experiments demonstrated that GEMS can alter to Fe-rich phyllosilicates (both serpentine and saponite species) at low temperatures (25°C) in alkaline solutions (pH 12-13) within less than 12 hours. This study therefore confirms that reaction rates for the hydration of amorphous silicate are at least two orders of magnitude faster than previously predicted by Nelson et al., (1987) and displayed here in Fig.1.

More recent experiments by Takigawa et al., (2019) exposed amorphous silicate analogues to water vapour (explicitly not liquid water) at low temperatures (-30°C to +50°C) over long durations (10-120 days) but found that alteration reactions cannot occur unless vapour temperatures are sustained above 0°C (25°C being their first above-zero run temperature in which alteration was observed). Abundant observations of comets have confirmed the presence of outgassing water vapour within cometary comae (e.g. Weaver et al., 1988; Russo et al., 2000; Feaga et al., 2007; Bockelée-Morvan et al., 2015). Therefore, primitive amorphous cometary silicates will be exposed to water vapour during perihelion passage. This likely forms a thin aqueous layer on silicate surfaces – which if heated sufficiently – could lead to surface aqueous alteration reactions (as demonstrated experimentally by Takigawa et al., 2019). Water vapour has a much longer orbital window than liquid water (generally forming once comets are within 3 A.U. of the Sun [Biver et al., 1997]) and thereby ensuring sustained interaction. However, vapour-facilitated alteration reaction rates are likely to be significantly slower than those caused by liquid water interaction, as demonstrated by comparing the <24hr liquid water alteration timescales seen by Nakamura et al. (2011) against the 100-1000hr vapour phase alteration timescales of Takigawa et al. (2019). Furthermore, because aqueously altered cometary dust is relatively rare, while vapour-silicate interaction should be ubiquitous, it is unlikely that vapour reactions play a critical role in the aqueous alteration of cometary materials. Instead, the limited evidence of aqueously alteration on only a small number of comets is best explained if liquid water is required before hydration reactions occur. A detailed investigation of vapour phase silicate interaction extends beyond the scope of this paper but requires future research attention.

4. Possible energy sources for the aqueous alteration on comets

The two leading hypotheses for the source of heat energy driving aqueous alteration (and thermal metamorphism) on hydrated chondritic asteroids are (1) planetesimal-scale high-energy impact events (Rubin, 2012; Lindgren et al., 2015; Vacher et al., 2018) and (2) the radioactive decay of short-lived isotopes (e.g. ^{26}Al, Keil 2000; McSween et al., 2002). Both mechanisms provide sufficiently high temperatures and sufficiently long durations, as defined by experimental and petrographic constraints from meteorite studies and are, therefore, consistent with the expected alteration environments of asteroids. For example, the alteration of CM chondrites appears to have reached temperatures as high as 300°C. These estimates are based on the O-isotopic fractionation signatures preserved in secondary phases, primarily carbonates (Guo and Eiler, 2007 [20-71°C]; Verdier-Paoletti et al., 2017 [50-300°C]; Vacher et al., 2019 [-10 to 250°C]). Aqueous alteration in CM chondrites occurred over exceptionally long durations, perhaps several millions of years (as inferred from ^{53}Mn-^{53}Cr dating by Lee et al., [2012]). However, the growth of individual crystals is likely to have been episodic in nature (de Leuw et al., 2009; Lee et al., 2012). Thus an impact heating scenario (for the CMs [at least]) is also capable of explaining the O-isotopic fractionation signatures, the weak correlation observed between the degree of aqueous alteration, and the strength of petrofabrics as well as the prevalence of crushed chondrules (Rubin, 2012; Hanna et al., 2015; Lindgren et al., 2015; Vacher et al., 2018).

In contrast to the thermal histories of asteroids, both radiogenic and impact heating may have been inefficient or entirely absent as heating mechanisms for cometary parent bodies originating in the cold outer solar system. This is because the parent bodies of comets are generally assumed to have formed in a low-density region of the early solar system, resulting in significantly fewer collisions and thus a greatly reduced impact energy for internal heating (Davidsson et al., 2016). Furthermore, cometary parent bodies are likely to have formed later than asteroids. This delayed growth would avoid appreciable thermal processing generated by the radiogenic decay of short-lived isotopes, primarily ^{26}Al whose half-life is just 0.73Ma (Podolak and Prialnik, 1997; Mousis et al., 2017). Choi et al., (2002) estimated that Kuiper Belt objects would have, in the best-case scenarios, achieved temperatures only as high as -93°C as a result of ^{26}Al decay. Additionally, this heating would be localised to the parent body's core, while the outer layers would have remained unheated. Similarly, Prialnik et al., (1987) argued that observations of outgassing at surprisingly large heliocentric distances (5.8-11.4 A.U.) which are currently attributed to the annealing of amorphous ice when comets first enter the inner solar system (Prialnik and Bar-Nun, 1990; 1992; Meech et al., 2009) – provides a clear constraint on the maximum parent body temperatures (T<-138°C) experienced by cometary parent bodies over their lifetimes.

Recent suggestions have, however, challenged this argument. There is growing recognition that asteroids and comets potentially form a continuum of objects with transitional properties (Hartmann et al., 1987; Gounelle, 2011; Nuth et al., 2019). Notably, some cometary parent bodies may in fact have originated in the inner solar system and experienced asteroidal processing (e.g. CM-like alteration induced by radiogenic or impact mechanisms). These bodies were later ejected outwards during the giant planet migration phase (Walsh et al., 2012). They would then have developed further during a second phase of volatile accretion, covering their asteroidal interior with a cometary cover (Meech et al., 2016; Nuth et al., 2019). Such bodies are termed Manx comets (named after a cat breed that lack tails) and are nearly inactive, either lacking a characteristic cometary tail or having a weak tail owing to their thin volatile covers (Meech et al., 2016)[1]. In these bodies phyllosilicates would be

[1] In the future, the classification of small bodies as either hydrous/ice-bearing or anhydrous may therefore serve as more meaningful grouping than asteroid and comet.

explainable simply as a product of their warm early alteration before subsequent residence in the outer solar system. However, Manx comets are expected to be relatively rare components of the solar system and not the most common type of comet. For example, among the 106 long-period comets studied by Meech et al., (2016) just 2 were found to have minimal activity and thus be potential Manx comets (Engelhardt et al., 2017).

Conversely, if both impact and radiogenic heating were indeed inactive on most cometary parent bodies, then an alternative model is required to explain the mild aqueous alteration activity expected in (some) comets (Noguchi et al., 2017). For example, aqueous alteration may have been a late-stage feature, occurring only once a comet enters the inner solar system and where perihelion heating by the Sun was able to warm the subsurface layers allowing liquid water to temporarily exist immediately prior to degassing and coma formation. Such a scenario would also be consistent with the preservation of amorphous ice until solar heating causes recrystallization and/or sublimation.

5. Can Perihelion heating generate subsurface liquid water?

To explore whether liquid water is viable requires consideration of the subsurface conditions inside comets as they approach perihelion. Solar radiant heating would need to generate sufficient subsurface pressure and temperature regimes over timescales on the order of hours, at least, if reactions with silicates are to occur. This short-term survival will be dependent on two factors (1) temperature and (2) pressure, as shown by the phase diagram of water, with the stability field of liquid water highlighted (Fig.2). For pure liquid water to be present the pressure and temperature at the triple point must be exceeded (T>0.01°C and P>611.2 Pa). We consider each variable in turn:

(1) Temperature: Surface temperatures for several comets over a range of heliocentric distances have now been measured by spacecraft using thermal infrared techniques. These include 1P/Halley by the Soviet space probe Vega-1 (Emerich, et al., 1986), 19/P Borrelly by NASA's Deep Space 1 mission (Soderblom et al., 2004), 9P/Tempel (Tempel 1) and 103P/Hartley by the NASA's Deep Impact mission (Groussin et al., 2013) and most recently, 67P/Churyumov–Gerasimenko by ESA's Rosetta mission (Tosi et al., 2019) (Fig.3). These empirical measurements, collectively define a power-law relationship between surface temperature and heliocentric distance (Fig.3) and demonstrate that surface temperatures between 0-120°C may be reasonably inferred for comets with perihelion distances <1.5A.U. The next logical question to consider therefore is how surface temperatures are related to subsurface temperatures?

Thermal conduction is the primary mechanism by which surface heat will migrate inwards through the comet's subsurface (although other processes such as gas-driven convection and radiative heat transfer may also be important, these are considered in detail below). Thermal conduction within comets is highly inefficient due to the presence of porous amorphous ice (Kouchi et al., 1992). Conduction is further inhibited by the presence of non-volatile dust-rich crusts that develop on comets as they survive multiple perihelion passes (Kömle and Steiner, 1992; Schulz et al., 2015; Quirico et al., 2015; Miles, 2016). Thus, comets have low thermal inertia, with quoted values typically given at $<50 WK^{-1}m^{-2}s^{1/2}$ (Fernandez et al. 2002; Lisse et al. 2005; Groussin et al., 2007; 2013; Davidsson et al., 2013; Shi et al., 2016) consistent with the measured thermal inertia for 67P ($85 \pm 35 WK^{-1}m^{-2}s^{1/2}$, Spohn et al., 2015). In consideration of these factors Wickramasinghe et al., (2009) also explored the possibility of perihelion-induced liquid water, using numerical modelling to estimate internal subsurface temperatures, based on a three-layer model (top: "burnt asphalt", middle: porous organic-rich crust and base: water-ice layer). This study concluded that solar radiant heating can penetrate to depths on the order of 1m. In their model, the overall relationship between surface and subsurface temperatures is described by an exponential relationship:

$$T_Z = Se^{(-AZ)} \qquad \text{(eq. 1)}$$

Where:
T_Z = internal temperature T at depth Z.
S = Surface temperature
A = the slope function (a constant), varying between 0.006 and 0.008 (here we use the avg. value of 0.007).
Z = depth within the comet (given in cm).

Using this model equation, we input the average temperature data from the five periodic comets with measured surface temperatures (1P, 9P, 19P, 67P and 103P), thereby allowing an approximation of their subsurface temperature profiles during perihelion (Fig.4). The model of Wickramasinghe et al., (2009) therefore suggests that temperatures >0°C may be attainable for subsurface depths <40cm in bodies with perihelia <1.5.A.U.

Alternative studies provide additional estimates on the heat transfer dynamics through a cometary subsurface. For example, direct observations of the comet 9P/Tempel allowed the production of a surface temperature map (generated prior to impact). This indicated that the penetration of surface heat is likely to be highly limited (Groussin et al., 2007), perhaps on scales of <10cm and thus less pronounced than in the model of Wickramasinghe et al., (2009). Similarly, empirical observations during the approach to 9P/Tempel Deep Impact noted the release of volatile H_2O (and CO_2) during early plume activity which appeared to originate from the immediate subsurface restricted to the centimetre to metre scale below the surface (A'Hearn et al., 2005; Thomas et al., 2008). This further supports the notion that solar radiative heating penetrates to limited depths. Thus, the formation of liquid water, if possible, will also be limited to depths of ~5cm<D<<1m.

Non-conductive heating: It is also worthwhile considering the role of non-conductive heat transfer within the comet's subsurface as these processes may provide additional non-negligible heating effects. Hu et al., (2019) explored the effects of radiative transfer and concluded that this is most efficient in the shallow subsurface (~5cm), during daytime, at small heliocentric distances and in materials with large pores. When compared against a purely conductive model radiative effects can increase temperatures by at least +20ºC (at a distance of 2 A.U. as modelled for 67P).

Other mechanisms are also possible. The sublimation of near-surface ice, for example, will generate water vapour under an elevated pressure. Porous media-flow of water vapour inwards through the pore network will also transfer heat inwards from the outer-layers, although this is generally considered inefficient (Kömle and Steiner, 1992). Alternatively, freeze-thaw behaviour during diurnal heating cycles may also enhance internal fracturing, allowing water vapour (or liquid water) to penetrate deeper along open conduits. Attree et al., (2018) modelled the fracture behaviour of 67P and suggested that cracks penetrating to depths of 0.25m into the surface are possible, consistent with the observations of polygonal-shaped crack networks exposed on the comet's surface. Crack networks in bodies which pass closer to the Sun than 67P are likely to penetrate deep and form more extensive networks. Temperatures may, therefore, be somewhat higher than those suggested by equation (eq.1).

Rotational period and spin axis orientation: Another major factor controlling the subsurface heating is the rotational period of comets. Temperatures fluctuate rhythmically on a diurnal cycle – the magnitude of which is greatest at the surface and decreases inwards. This temperature gradient is also affected by a thermal time-lag due to the low thermal inertia of cometary materials (Wickramasinghe et al., 2009; Farnham et al., 2013; Shi et al., 2016). For example, Farnham et al., (2013) observed that jetting activity on 81P/Wild 2 continued for up to 4 hours after rotation of the jets into darkness. A

comet's rotational period therefore has significant control on the duration of subsurface heating and the length of time liquid water can survive. Shorter rotational periods will necessarily result in shorter episodes at peak temperatures (Wickramasinghe et al., 2009; Farnham et al., 2013; Shi et al., 2016).

Wickramasinghe et al., (2009) modelled a 40-hour rotation period (equivalent to that of 9P/Tempel [Groussin et al., 2007]) and concluded that peak temperatures will be maintained for approximately 10 hours (one quarter day-length, Wickramasinghe et al., 2009). This timeframe is close to the maximum rotational period measured for JFCs, which typically range between 8.1 hours and 17.2 hours (the interquartile range of rotational periods of 37 comets, calculated from the data given in Kokotanekova et al., [2017], here displayed in Fig.5). Thus, for most comets which rotate faster, the depth of heat penetration will also be shallower and the duration of heating shorter. Average timescales for subsurface heating in periodic comets may therefore last just 2-5 hours per diurnal cycle. However, the total duration over which liquid water could form (across repeated melting/re-freezing events) will be a product of multiple daily cycles as the comet passes through perihelion.

Comets typically display significant activity for 1 month prior and 1-2 months after perihelion passage, attesting to appreciable subsurface heating during this time (Lara et al., 2015; Snodgrass et al., 2016; Pätzold et a., 2019). For example, 67P passed within 1.24 A.U. of the Sun on 13/08/2015 but displayed enhanced coma activity for ~2 months with peak activity 2 weeks after perihelion (Snodgrass et al., 2016). This indicates that the subsurface has a strong thermal lag and that average temperatures increased slowly on week-long timescales creating a seasonal heating effect, even where diurnal temperatures fluctuated over much shorter timescales (the rotational period of 67P is just 12.76 hours). Thus, it seems unavoidable that sustained subsurface heating occurs through the retention of heat throughout the (short) night-time cooling phase in comets with stable rotating states and average rotational periods. Peak temperatures could therefore be achieved either through combined melting/re-freezing cycles or by a slow increase in subsurface temperature over seasonal timescales. In both scenarios these conditions could exceed the 24-48 hours required for the aqueous alteration of highly susceptible GEMS.

Comets can also have "tumbling" rotational states in which the orientation of the rotational axis varies chaotically over time. In addition, a significant proportion of comets have stable rotational states but high obliquity (axial tilt) resulting in strong seasonal contrasts and perihelion periods in which one hemisphere experiences an enhanced heating effect due to longer exposure to solar heating. Among the asteroid population most slow rotators (with periods in the 10's to 100's of hours) commonly have tumbling rotational states (Harris and Pravec, 2005). Although the prevalence of chaotic rotational states among periodic comets is poorly constrained, both stable and chaotic states have been observed for several bodies. Notably, 1P and 67P have stable rotational axes, while both 17P and 46P have chaotic states in which the axis of rotation changes even over the course of a single orbital period (Mysen, 2004). Likewise, the rotational axis of 2P/Encke appears to have changed significantly over the last 300 years (~100 orbits) with obliquity reaching an extreme value of 103º in ~1850 and later remaining stable at ~70º between 1924-1984. During this time the spin axis was directed towards the Sun, leaving a polar hemisphere continuously exposed during perihelion passes (Whipple and Sekanina, 1979; Sekanina, 1988; Sanzovo et al., 2001). Similarly, the long-period comet C/1995 O1 (Hale-Bopp) also had an extreme axial tilt of 83º during it's perihelion pass in 1996-97 (Licandro et al., 1997). The effects of rotational period creating diurnal heating cycles may become irrelevant in bodies with Sun-directed rotational axes, either due to tumbling rotation or high obliquity. In such situations subsurface heat transfer is maximized generating more than sufficient time for alteration reactions to proceed.

(2) Pressure: Internal gas pressures are generated by the sublimation of volatiles and super-volatiles. The release of these gases raise local pore pressure as the gas release rate from mineral phases exceeds the gas escape rate from the comet's subsurface (Prilank and Bar-Nun, 1990; Kömle et al., 1992; Almedia et al., 2016). For liquid water to form, pressures must exceed the water triple point (Fig.2), which requires pressures above 611Pa (at temperatures of 0°C) for pure water, and lower pressures for impure/saline water (e.g. ~300 Pa at 2 mol% NaCl solution, Fig.2 and Feistel et al., 2008).

The existence of dusty ice-depleted crusts on comets which have been subject to multiple previous perihelion degassing passages (Kömle et al., 1992; Wickramasinghe et al., 2009; Quirico et al., 2015) and the presence of "dirty" ice, intermixed with other components appear to play a crucial role in the formation of internal gas pressures.

Early estimates of cometary internal pressures where made by Prialnik and Bar-Nun (1990) using numerical modelling to study the evolution of a comet's interior with a 1P/Halley-like orbit over multiple perihelion passes. They assumed as a starting point a nucleus composed of cold porous amorphous ice containing 10% trapped carbon monoxide and concluded that internal gas pressures could potentially reach values as high as 2MPa when sublimating gases (released upon crystallization of amorphous ice) become trapped. In their model peak pressures occur within 20m of the cometary surface. However, Prialnik and Sierks (2017) produced a significantly revised model of internal gas pressures and concluded that cometary peak pressures may be as low as 2Pa. This revised estimate is constrained by the low material strength (especially under tensional stress) of cometary dust aggregates, whose connections between clusters are exceptionally weak (Asphaug and Benz, 1996; Blum et al., 2014).

Independently, Kömle et al., (1992) performed experimental studies heating cometary analogues composed of porous fine-grained ice covered by a dark dust mantle composed of graphite and/or SiC – representing a non-volatile crust covering an unheated pristine interior. They noted that the addition of even small quantities of impurities radically changed the behaviour of the pore pressure within ice structures. During sublimation the subsurface evolves significantly because small light-weight particles are easily redistributed to block pore interconnections, allowing pressure build-up and creating larger pores with fewer interconnections. However, these higher pressures were estimated to reach just 50Pa while also being restricted to a very thin boundary layer within the ice, most likely on the order of millimetres to centimetres (Kömle et al., 1992). In contrast, deeper in the structure pore pressures were consistent with the equilibrium vapour pressures.

A similar mechanism of raised internal gas pressure was also proposed by De Almedia et al., (2016) – termed the pressurized obstructed pore model and based on outburst activity observed for 17P/Holmes. They suggested that after an initial heating phase and the sublimation of water-ice to form water vapour, some of this vapour could refreeze before it escapes, thereby blocking pore space and increasing the comet's tensile strength in or near the outer crust region. This would have the effect of preventing the escape of newly released subsurface volatile gases. These trapped gases would then ultimately be released in explosive episodes. Such a model could explain the observed pre- and post-perihelion sudden explosive outburst activity. They estimate that internal gas pressures on the order of 1kPa are required to facilitate rupture of the icy crust (De Almedia et al., 2016), while Reach et a., (2010) estimated that the same explosion requires tensile strengths on length scales >10m to be 10kPa<t<200kPa.

An alternative model for the evolution of cometary interiors was proposed by Miles (2016) and explored how sublimating volatile species interact and could potentially work synergistically to produce runaway heating and pressure increases. Miles (2016) suggests that an initial heating episode results in the release of super-volatiles which raise the local pore pressures sufficiently to stabilise

simple hydrocarbon liquid phases, primarily liquid methane. Subsequent volatile gases which are released then dissolve in this liquid methane forming a complex organic solution. Since these reactions are exothermic this process acts as an internal heat "engine" and causes a progressive rise in internal gas pressures and temperatures. Under this scenario it may therefore be possible to reach pressure-temperature conditions far in excess of that required for liquid water stabilisation. Miles (2016) estimates maximum pressures as high as 200kPa.

Although, the internal gas pressure estimates for cometary interiors vary widely, most studies conclude that gas release from volatiles (when the comet approaches perihelion) occurs at rates higher than the gas escape rate, primarily due to pore blocking below their non-volatile crusts. Thus, the maximum internal pressures of comets are instead directly dependent on their tensile strength – equivalent to their ability to withstand pressure before rupturing explosively. Estimates for cometary tensile strength are more easily determined.

A rotating object is held together by material strength and gravitational forces. These resist the action of centrifugal force that would otherwise catastrophically disrupt the object. Since centrifugal forces are dependent on the rotation rate, fast spinning bodies and rotational breakup events provide unique opportunities to investigate the tensile strength of comets. Such studies require accurate measurement of a body's size, shape and rotational period prior to breakup as well as estimates of the object's density and structure. They typically conclude that comets have low tensile strengths (20-400Pa, Lisse et al. 1999; <100Pa Davidsson, 2001). Likewise, the fragmentation of D/1993 F2 (Shoemaker–Levy 9) by tidal forces as the comet passed within Jupiter's Roche limit acted as a natural experiment testing the tensile strength of a comet. The early breakup of Shoemaker–Levy 9 suggested the comet had a loose aggregate structure and a low tensile strength (>270Pa, Greenberg et al., 1995). By contrast, new observations from the Rosetta mission provide empirical evidence from an "*in-situ*" comet. The presence of landslides and exposed steep cliffs formed under micro-gravity conditions also suggest that 67P has very low tensile strength, potentially in the region of 3-15Pa, although upper maximum values of 150Pa over 30m length scales and 1150Pa over 1m scales are quoted in Groussin et al. (2015). Conversely, some of these slope features preserve evidence of fracturing (Sierks et al., 2015), which necessarily requires non-zero tensile strengths. Alternatively, more direct estimates can be made from the behaviour of the Philae lander, which hit the comet's surface and encountered a higher-than-expected compressive strength, estimated to be in the range 4-7MPa by Spohn et al., (2015) based on the incomplete penetration of the MUPUS (Multipurpose Sensors for Surface and Sub-Surface Science) hammer. Since compressive strengths are typically an order of magnitude higher than tensile strengths this suggests that the 67P parent body may support tensile strengths as high as 400-700kPa.

Data from 67P/Churyumov–Gerasimenko measures a "fresh" and dynamically young comet (Maquet, 2015). In contrast, the tensile strength of cometary materials may also evolve with heating, for example due to the formation of re-frozen ice in the comet's upper layers (Feaga et al.,2007; De Almedia et al., 2016). Alternatively, if water vapour can lead to the hydration of silicates (Takigawa et al., 2019) then the formation of interlocking clay minerals could also increase cometary tensile strength by binding grains together. Initial formation of hydrous products from water vapour alteration, even though incipient, is likely to lead to increases in strength owing to the formation of hydrated minerals as a cement between touching mineral grains (Rhim, 2011). Similar behaviour is observed in terrestrial sediments during early diagenesis where partial cements form on menisci between mineral grains – this is particularly the case in beach sands where small amounts of cement growth rapidly indurate unconsolidated sediment (Garrison, 1969). Observations of 67P/Churyumov–Gerasimenko may not, therefore, provide the most appropriate values of tensile strength in relation to liquid water generation since phyllosilicates were not detected on this comet. Alternative estimates for tensile strength have been derived from cometary meteoroids, they have values between 10kPa from pristine comets and significantly higher values of 80kPa for evolved comets (such as the taurids

from 2P/Encke) (Trigo-Rodriguez and Blum, 2009). These values support the notion that tensile strength increases with the time spent in the inner solar system. The tensile strength of cometary materials, therefore, may exceed the ~300-600Pa required for liquid water stabilisation and demonstrate that conditions suitable to liquid water could be supported in the cometary interior without disruption (Fig.6 summarizes temperature and pressure estimates for periodic comets discussed in section 5).

6. Alternative mechanisms for the existence of liquid water

In section 5 we considered the viability of pure liquid water within a cometary subsurface forming under equilibrium conditions. However, there are additional factors that could facilitate the generation and survival of liquid water at lower temperatures and lower pressures under dynamic conditions. These include (1) the addition of salts to form cryobrines (2) the existence of nano-scale liquid water films and (3) the formation of liquid water under non-equilibrium conditions.

(1) Although pure water requires conditions to exceed T=0.01°C and P=611.2Pa, impure water can exist at lower temperatures and pressures owing to the effects of freezing point depression (Fig.2). For simple H_2O-NaCl systems, moderate quantities of salt can lower the eutectic (-8 °C) and half the required vapour pressure (~300Pa) (Feistel et al., 2008). In the extreme case concentrated cryo-brines containing both Cl-bearing and S-bearing salts can support remarkably low eutectic points, stable down to temperatures as low as -63°C and pressures as low as 100 Pa (Brass, 1980; Chevrier and Altheide, 2008; Möhlmann, 2011). The relevance of such highly concentrated solutions for cometary systems remains unknown but seem likely, given that both sulphur and chlorine are liberated early in the aqueous alteration of chondritic materials; sulphur is released from GEMS and GEMS-like phases, while chlorine is leached from chondrule glass (Brearley and Jones, 2018). These highly saline conditions may therefore be present after an initial period of liquid water formation, where an actively evaporating solution leaves behind an increasingly concentrated brine. In such cases, salt concentration by evaporation would act to increase the length of time at which liquid water remains through freezing point depression.

(2) At the micron to nano-scale, small quantities of undercooled interfacial water can form and survive where the attractive pressure of van der Waals forces between mineral grain surfaces acts to stabilize water films (Rietmeijer, 1985; Möhlmann, 2011). This occurs because intermolecular forces between grains generate sufficient pressure to cause freezing point depression. Thus, liquid water will be generated (and maintained permanently) where silicate and ice grains are in contact. Experimental studies demonstrate that a thin layer (>6Å) of this surface water can never be frozen even as temperatures approach absolute zero (Anderson, 1968; Rietmeijer, 1985). Furthermore, the thickness of the adsorbed water varies dependent on temperature and mineral species, with higher temperatures (close to the system's melting point) and hydrophilic minerals capable of maintaining thicker films. In fine-grained mixed mineral-ice assemblages liquid water content, generated by interfacial forces, can reach up to 10% of the total water present (Möhlmann, 2011).

Cometary micrometeorites are composed of submicron mineral assemblages with high porosities. Some of this porosity would have been filled by water-ice, creating situations in which interfacial liquid water would form and could theoretically perform aqueous alteration reactions (Rietmeijer, 1985). However, these conditions will necessarily occur at low temperatures, below the freezing point of the water-ice system (for the ambient pressure conditions) and thus reaction rates will be exceptionally slow (perhaps on the order of 10^4-10^6 years, Rietmeijer, 1985). These long timescales are not relevant for perihelion-induced alteration mechanisms but potentially important processes in long-period comets. Furthermore, even where reactions are viable their extent is also limited. In the case of silicate alteration reaction rates slow significantly once the exposed mineral face has been altered. This is because the reaction products create a barrier to diffusion, limiting further alteration below the

exposed surface (Rietmeijer et al., 2002; Le Guillou et al., 2015). Thus, Interfacial liquid water may produce localized alteration, along grain surfaces in direct contact with water-ice. However, such conditions could not generate extensive aqueous alteration nor are they likely responsible for the moderately altered chondritic porous micrometeorites which do not appear to show correlation between pore space proximity and alteration extent. (Fig.4, Noguchi et al., 2017). Instead interfacial water may be capable of generating subtle nanophase alteration products like the ~300nm amphibole grains suspended within a GEMS host that were described by Busemann et al., (2009 [Fig.8]) within a cometary micrometeorite.

(3) For time-variable conditions the temporary existence of liquid water is also possible at temperatures and pressures well beyond the triple point. This was demonstrated experimentally by Kömle et al., (2018) where a melting probe slowly penetrated into a water-ice layer under ambient pressures of just 20Pa and temperatures between -10ºC to -30ºC. Such situations might be relevant to scenarios where a cometary parent body is impacted, either on the micron-scale by high-speed cosmic dust or on larger scales by centimetre to metre sized objects. Temperature and pressures generated would then easily exceed triple point requirements. However, the lifetimes of liquid water under such conditions are unlikely to survive longer than a few minutes. Non-equilibrium liquid water is therefore not expected to be a significant mechanism for aqueous alteration reactions.

7. Is alteration possible before dust shedding?

Previously we explored how heating over multiple diurnal cycles could produce repeated melting and re-freezing events as well as a slow increase in the average subsurface temperature. However, cumulative heating will only be possible if the erosion rate at the comet's surface near perihelion is sufficiently slow for alteration to occur before the shallow subsurface is ejected into the coma. It is therefore critical to consider how much material may be lost from the comet's surface during a single perihelion pass.

Estimates of the mass loss rate for comets over a single perihelion pass are variable, reflecting our limited knowledge of the process as well as the complex set of parameters which combine to control the mass loss rate. Based on the Deep Impact observations of 9P/Tempel Thomas et al., (2008) argued that the peak erosion rate for periodic comets can reach rates as high as one thermal skin depth per cometary day. This translates to a loss of around 3m per orbit (for 9P) equivalent to approximately 100 thermal skin depths (assuming a skin depth of just 2-3cm). However, a comet's surface erosion rate is strongly dependent on several factors, not just the thermal skin depth but also the depth from which volatile gas emissions occur as well as the thickness of the non-volatile cover. As these factors increase the rate of erosion may be slowed by a factor of ten. Alternative estimates generally suggest lower erosion rates. Bertaux (2015) estimated a loss rate of 1.0 ± 0.5m per orbit for 67P using space telescope data collected over its three previous orbits (1996, 2002, and 2009) prior to arrival of the Rosetta spacecraft. In contrast, during the 2015 perihelion Rosetta data suggest that 67P lost just 0.1% of its nucleus mass (Pätzold et al., 2019) translating to an erosion rate of 0.44-0.55m averaged across the surface (Keller et al., 2017). Meanwhile Sanzovo et al., (2001) estimated relatively modest erosion rates for two comets: 6P/d'Arrest (~0.5m per orbit) and 2P/Encke (~0.3m per orbit). In Fig.7 we compare how differences in the erosion rate (100cm, 50cm, 30cm and 10cm per orbit) and the duration over which the total surface loss occurs (x-axis titled as "perihelion duration" [and given in weeks]) affect the averaged surface erosion rate. This demonstrates that even at moderate-to-high erosion rates of 100cm/perihelion and a short duration over which this loss occurs (1 week), the outermost 10cm of a comet can survive for ~16.8 hours (Fig.7). Furthermore, as the duration over which surface loss occurs is increased or the erosion rate decreases, this outermost layer survives for much longer. These calculations suggest that in some periodic comets the conditions of liquid water could be maintained long enough to result in the aqueous alteration of GEMS to primitive phyllosilicates.

8. Spectroscopic observations of phyllosilicate-bearing comets

Ground-based and space-based remote sensing observations of aqueous alteration products in comets are somewhat controversial. Hayward et al., (2000) and Kelley and Wooden (2009) failed to detect hydrated spectral signatures associated with phyllosilicates in two comets, suggesting these are not major components on cometary surfaces. If aqueous alteration minerals are present, they are therefore highly limited in extent. This is consistent with the conclusions from microanalysis studies of cometary micrometeorites. When phyllosilicates are present, they occur at low concentrations and have poorly crystalline structures (Noguchi et al., 2017). However, two other comets (9P/Tempel and Hale-Bopp [C/1995 O1]) have reported detections of both carbonate and (probable) phyllosilicate (Lisse et al., 2006; 2007) and notably both comets passed close to the Sun (1.542 and 0.914 AU respectively). The carbonate emission especially occurs in a "clean" part of the mid-infrared spectrum unconfused by other possible sources of emission, Additionally, outburst jets from 1P/Halley showed evidence of carbonate spectral signatures (Bregman et al., 1987). Since outbursts are characterized by sudden enhanced dust release without concurrent increases in gas production, they may be associated with landslide activity (Pajola et al., 2017) releasing materials from the immediate subsurface. Bussemann et al. (2009) added support to the presence of carbonate in comets through the discovery of carbonate grains in IDPs collected during the Pi Puppids meteor shower and associated with comet 26P/Grigg-Skjellerup – this makes the current evidence for cometary carbonates relatively strong.

Phyllosilicates on 9P/Tempel: NASA's *Deep Impact* mission collided with the nucleus of comet 9P/Tempel and generated a large plume of material excavated from the comet's subsurface (generating a crater ~200m in diameter and removing material potentially to a depth of 5m [Schultz et al., 2013]). Spectral observations by the Spitzer Space Telescope interpreted by Lisse et al., (2006; 2007) suggested the presence of both carbonates (occurring at ~5% of the ejecta by surface area) and phyllosilicates (composing ~8% of the ejecta by surface area). Since both these minerals are strongly associated with aqueous alteration, this provides a compelling case that liquid water existed within the subsurface of 9P at some point, either during the early solar system, or recently due to perihelion heating. Although the detection of a phyllosilicate spectral signature among the impact debris of 9P remains controversial (e.g. Harker et al., 2005) its presence would be consistent with a subsurface liquid water generation model.

Dynamical modelling suggests that 9P/Tempel's orbit evolved during the 1600's after a close-approach with Jupiter, resulting in a significant decrease in the body's perihelion distance from ~3.5 A.U. to 1.5 A.U. (Yeomans et al., 2004). This would significantly increase the comet's subsurface heating and resulting activity, ultimately leading to its discovery in 1867.

Phyllosilicates on Halle-Bopp: Hale-Bopp is another comet in which a probable phyllosilicate spectral signature has been identified. Lisse et al., (2007) argue for abundances around 18%. In contrast, Wooden et al., (1999) could not rule out the possibility of phyllosilicates in the spectra of Hale-Bopp but limited their abundance to <1%. Similarly, Hale-Bopp's orbital history is more uncertain. It is dynamically young but with an exceedingly long orbital period, approximately 2500 years. Hale-Bopp may have been perturbed by close-approach with Jupiter approximately 4200 years ago (2215 BCE), which led to a significant reduction in its perihelion down to ~0.9A.U. (Mardsen, 1997). Hale-Bopp has likely experienced far fewer close perihelia than 9P/Tempel although its single known pass generated significant cometary activity resulting in sufficient brightness for unaided naked eye observations over 18 months (1996-1997, de Almeida et al., 2009).

To date, 9P/Tempel and Hale-Bopp remain the only comets with potential phyllosilicate spectral signatures and thus evidence of pronounced aqueous alteration. Tempel 1 has resided within 225 million km of the Sun (~1.5 A.U.) and remained in this close-approach orbit for over 400 years (equivalent to more than 70 perihelion passes) – providing a long duration over which repeated surface heating of the comet's outer layers could trigger aqueous alteration. For comparison, the anhydrous comet WILD 2 (81P/Wild) was only brought into the inner solar system recently, after a close-approach with Jupiter in September 1974 (Królikowska and Szutowicz, 2006). Thus, when this body was sampled by the STARDUST mission in 2006, relatively few perihelia had passed (~5 orbits), limiting the potential for radiative heating. Similarly, 67P/Churyumov–Gerasimenko's orbit evolved following a close-approach with Jupiter in 1959, leading to a significant reduction in its perihelion distance from 2.7A.U. to 1.3A.U. (Maquet, 2015). Thus, the lack of hydrated phyllosilicates on 67P is expected given its (solar-facing) daytime temperatures do not appear to exceed -45°C (Tosi et al., 2019) and it has experienced relatively few (<10) perihelion passes at this closer distance. This suggests that perihelion-induced alteration can only be effective for comets which are thrown into the inner solar system and spend several perihelia close (<1.5A.U.) to the Sun.

9. Implications – How many comets are affected by perihelion-induced liquid water formation?

Most known periodic comets have perihelion distances <4A.U. (Fig.8, 348 bodies or >95%, Minor Planet Center, 2019). If alteration by liquid water is facilitated by an initial phase of vapour-driven alteration in order to increase a comet's tensile strength and lower surface permeability thereby allowing the comet to sustain higher internal gas pressures sufficient for the stabilization of liquid water, then the initial stages of alteration are likely to begin at temperatures of ~0°C. The data in Fig.6 suggest that this threshold is met between 1.0-1.5 A.U. Using a threshold of 1.5. A.U. suggests alteration might occur on approximately 91 known periodic comets (24.8% of the known population). Alternatively, if a threshold of <1 A.U. is required then approximately 35 known periodic comets (9.5% of the population) may be affected by this mechanism. However, because rotational properties also appear to exert a strong control, these two factors act together to prevent perihelion-induced alteration being a widespread phenomenon among the periodic comet population. Today the rotational properties of most periodic comets are unstudied. This makes estimating the number of bodies affected by this alteration mechanism difficult. Assuming one third of periodic comets have either a high obliquity (creating a sun-directed hemisphere) or slow rotational period, and that distances <1.5 or <1.0 A.U. are required, this suggests that 3-9% of periodic comets may be able to generate subsurface liquid water during perihelion and perform aqueous alteration reactions.

Considering the extremes, eight known periodic comets pass within 0.5A.U. of the Sun. They include 249P/LINEAR, 23P/Brorsen-Metcalf, 2P/Encke and 96P/Machholz as well as four SOHO (Solar and Heliospheric Observatory) comets (321P/SOHO, 322P/SOHO, 323P/SOHO and 342P/SOHO). Comets which pass exceptionally close to the Sun are termed sungrazers although the strict definition requires perihelia of ≲0.014 A.U., while a looser definition of "sunskirters" is used to describe comets identified by the SOHO spacecraft, which by necessity of their discovery method must pass close to the Sun (<<0.5 A.U., Battams and Knight, 2017). By May 2016, there were 3138 sunskirters, recently discovered, with poorly-constrained orbits and not currently assigned as "periodic" comets due to the lack of a second observed perihelion pass (or second apparition) (Battams and Knight, 2017). The sunskirters are primarily members of the Kreutz comet family, characterised by perihelia <2 solar radii, high orbital inclinations (i∼140◦) and long orbital periods. They may represent a single large parent body which broke up during a close-approach due to extreme tidal forces (Davidsson, 2001; Sekanina, 2002). Comet 2P/Encke as well as the sunskirting comets are ideal candidates for perihelion-induced

aqueous alteration, representing the most likely candidates in which to detect advanced alteration on a cometary petrology.

Sourcing micrometeorites to Earth: Finally, we note that numerous periodic comets with small perihelia (<1.4A.U.) are major dust-producing bodies associated with active meteor showers (perhaps as many as 42 candidate comets, Jenniskens, 2008). Notably this population includes the Pi Puppids linked to 26P/Grigg-Skjellerup whose perihelion is 1.1 A.U., the Draconids linked to 21P/Giacobini–Zinner whose perihelion is 1.038 A.U., the Perseids linked to 109P/Swift–Tuttle whose perihelion is 0.96 A.U and the Orionids and Eta Aquariids linked to 1P/Halley whose perihelion is 0.586A.U. (Jenniskens and Jenniskens, 2006; Jenniskens, 2008). In addition, the active asteroid 3200 Phaethon – the target of JAXA's planned DESTINY+ mission – also has an exceptionally small perihelion distance (just 0.14A.U) and is likewise associated with the Geminids meteor stream (Jewit and Li 2010). Estimated surface temperatures near perihelion may reach >900ºC based on numerical modelling (Chaumard et al., 2012). This large group of comets are predominantly dormant bodies, which no longer experience major cometary activity but remain associated with their daughter meteoroid streams (Jenniskens, 2008). By virtue of this association between meteor showers and dormant near-Earth comets, they will clearly contribute significantly to the sources of micrometeoroids reaching Earth (Jenniskens 2008). However, much of this dust will have high entry velocities owing to their eccentric orbits (generally between 25-70kms^{-1}, Younger et al., 2012) and thus only a small fraction of grains from this population – those with the most favourable entry conditions (small sizes and low entry angles) – will survive atmospheric entry (Flynn, 1990; Love and Brownlee, 1991) to be recovered either in the stratosphere by high-altitude collection missions (Flynn, 1994) or from the Earth's surface (e.g. in Antarctic snow) and subsequently analysed. However, a micrometeorite suspected to belong to the Pi-Puppids meteor shower (~19kms^{-1}, Vaubaillon and Colas, 2005), associated with 26P/Grigg–Skjellerup was recovered and studied by Busemann et al., (2009) – this particle contained both carbonates and amphibole (commonly considered secondary alteration minerals). Thus, the relatively rare mildly altered chondritic porous micrometeorites described by Noguchi et al., (2015; 2017) and ultracarbonaceous micrometeorites (Yabuta et al., 2017) could be direct samples of these near-Earth heated comets.

In contrast, cometary dust originating from more distant comets, those with larger perihelion distances and which have not experienced perihelion-induced aqueous alteration are likely to supply significantly more dust to Earth's surface due to a strong survivorship bias. This low eccentricity long-period population produce cosmic dust whose orbits are progressively circularized, evolving to low eccentricities and lower speeds (relative to Earth's orbit) meaning that they are more likely to survive atmospheric entry and are thus expected to appear more abundant in micrometeorite collections (Nesvorný et al., 2010; Carrillo-Sánchez et al., 2015; 2016). This effect could generate an overabundance of cosmic dust from unaltered comets among our micrometeorite collections.

10. Conclusions

Nominally anhydrous chondritic porous micrometeorites and ultracarbonaceous Antarctic micrometeorites are widely considered to be samples of comets. Some of these particles show evidence of mild parent body aqueous alteration (Nougchi et al., 2015; 2017; Yabuta et al., 2017), characterised by variable degrees of hydration resulting in the conversion of amorphous GEMS (primitive solar system condensates) to low crystallinity Fe-rich phyllosilicates. This incipient alteration, without further processing requires extremely short exposure to liquid water, most likely on timescales <24hrs, under mildly alkaline conditions (>pH8) and at low temperatures (≃0°C), as demonstrated by experimental studies (Rietmeijer et al., 2004; Nakamura-Messenger et al., 2011). In

contrast, in-situ observations of comets from spectroscopic telescopes (Kelley and Wooden, 2009) and space missions (Zolensky et al., 2006; 2008) conclude that cometary mineralogies lack evidence of phyllosilicates and are anhydrous – with the possible exception of 9P/Tempel and Hale-Bopp (Lisse et al., 2006). Heat sources conventionally considered responsible for aqueous alteration in asteroidal settings – namely radiogenic heating (Keil, 2000; McSween et al., 2002) and impact heating (Rubin, 2012; Hanna et al., 2015; Lindgren et al., 2015; Vacher et al., 2018) – are expected to be unsuitable mechanisms for alteration on late-formed outer solar system cometary parent bodies (Davidsson et al., 2016; Mousis et al., 2017). Thus, a different energy source is required to explain the observed alteration of cosmic dust.

We explored the viability of perihelion solar radiative heating as the energy source for aqueous alteration. This was previously suggested by Rietmeijer et al., (2004); Wickramasinghe et al., (2009), Ohtsuka et al., (2009) and Nakamura-messenger et al., (2011). Using recent experimental work, numerical modelling, space mission data and microanalysis studies, we explored whether the short-term generation of liquid water within the cometary subsurface during close-approaches to the Sun was possible. We conclude that solar radiative heating may be capable of generating liquid water in a comet's immediate subsurface for selected bodies with favourable conditions.

Based on the spacecraft-measured surface temperatures of comets 1P, 9P, 19P, 67P and 103P and their relationship with perihelion distance we demonstrated that bodies orbiting within <1.5 A.U. of the Sun can generate sufficiently high temperatures for liquid water to form in their immediate subsurface (at depths <40cm and likely <10cm). In contrast, whether sufficient pressure can be generated to stabilize liquid water remains uncertain. Previous studies have suggested a wide range of internal gas pressures, ranging over 5 orders of magnitude (1-700kPa). Alternatively, if we assume that the presence of explosive eruptions, as observed for several comets (Prialnik and Bar-Nun, 1992; de Almeida et al., 2016) is evidence that gas pressures can exceed the tensile strength of cometary material, which are generally on the order of 1000's of Pascals (Trigo-Rodriguez and Blum, 2009; Spohn et al., 2015), this suggests sufficient pressure could be generated.

Based on orbital data, approximately 9-24% of periodic comets pass within 1.0A.U. or 1.5 A.U. of the Sun. This provides an upper limit to the total number of bodies that may be affected by perihelion-induced heating. However, because many of these bodies are expected to have stable rotational axes and short rotational periods (<20 hours), subsurface heating durations in most comets may be too short to produce appreciable alteration. Instead, we predict that perihelion-induced aqueous alteration is likely only effective in comets with small perihelia and favourable rotational states (slow periods or Sun-directed axes). Given these limitations we predict that this mechanism should affect 3-9% of the current periodic comet population.

However, the fate of all comets is either evaporation, collisional disruption or ejection from the solar system. Many of the known periodic comets currently with distant perihelia are likely to be perturbed inwards, entering the zone of viable perihelion-induced aqueous alteration. On longer timescales, the inner solar system comet population is continually renewed by comets sent from the Kuiper belt and Oort cloud, providing a steady stream of material to replace those evaporated by the Sun. Thus, many more comets than those currently inside the potential zone of alteration will be affected, making this mechanism an important process in the end-stages of comet lifetimes.

Today, comet 2P/Encke represents an ideal candidate for perihelion-induced aqueous alteration reactions, having a small perihelion (~0.3 A.U.), a short orbital period (3.3 years) and a chaotic rotational state in which the Northern hemisphere is known to have been exposed continuously to solar heating for multiple orbital periods for over at least 100 years (Whipple and Sekanina, 1979). Furthermore, 2P/Encke is the parent body of the Taurids meteor shower and therefore sources

abundant cometary dust to Earth, raising the probability that aqueously altered cometary micrometeorites derived from a solar-heated body should be present among micrometeorite collections.

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11. List of figures and tables

Fig.1. Reaction rate kinetics relevant to the aqueous alteration of GEMS within a cometary subsurface. This plot displays an empirically determined temperature-dependence relationship for the hydration of amorphous Mg-SiO "smokes". The measured reaction products are sepiolite (a complex partial chain phyllosilicate). Data were taken from Nelson et al., (1987). However, we note that the absolute reaction times needed for the hydration of naturally-occurring GEMS to form primitive phyllosilicates (serpentine/saponite) are likely to be significantly shorter than the reaction times displayed here – perhaps two orders of magnitude shorter, as demonstrated by the alteration of anhydrous GEMS in Nakamura et al., (2011). Despite this duration discrepancy the temperature dependence relationship is likely accurate. The red and blue lines reflect the decay and growth of different spectral features as measured by IR spectroscopy.

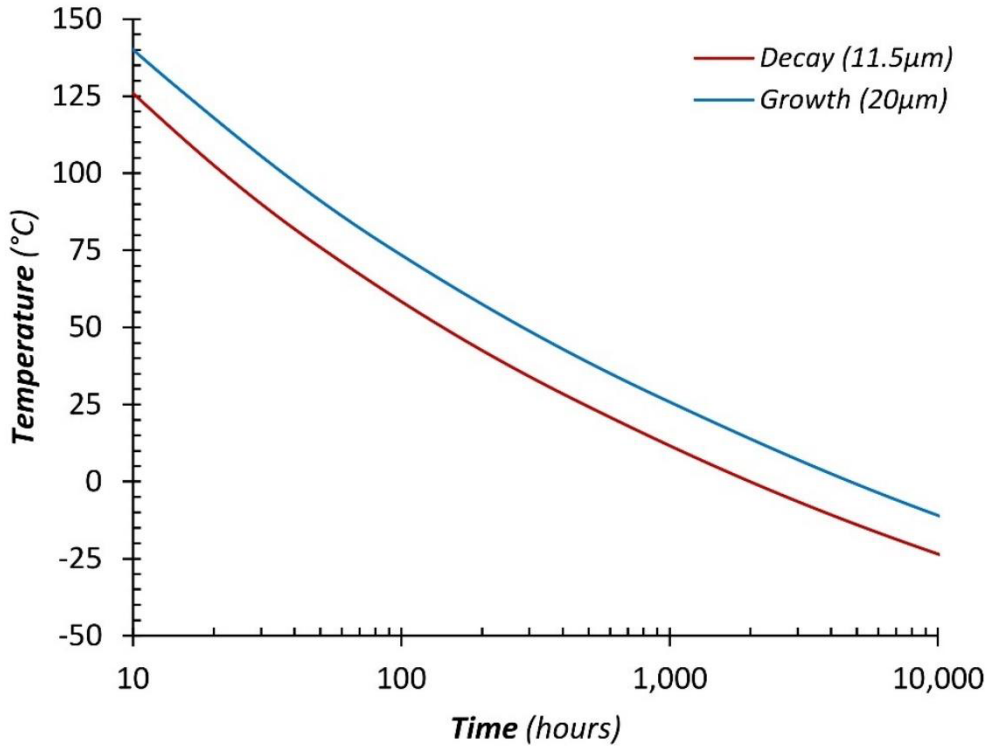

Fig.2. Water-ice phase diagram illustrating the action of increasing salinity (higher concentration NaCl solutions [red lowest concentration, green highest concentration]) on freezing point depression. Impure water has a significantly lower temperature and vapour pressure than pure water. Cometary water is unlikely to be pure, but instead mixed with a range of salts, potentially NaCl as well as sulfate salts. (Data from Feistel et al., 2008).

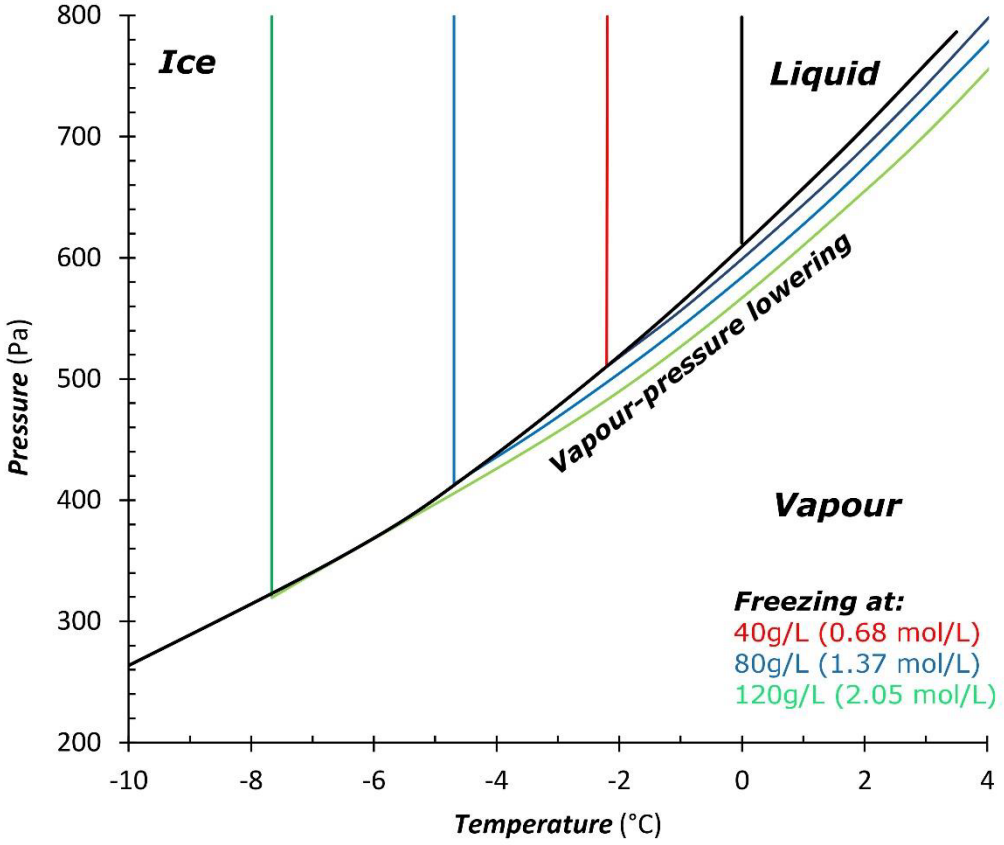

Fig.3. Measured comet surface temperature vs. heliocentric distance for five periodic comets (1P, 9P, 19P, 67P and 103P). Data derived from: Emerich, et al., (1986), Soderblom et al., (2004), Groussin et al., (2007; 2013) and Tosi et al., (2019). Black points mark their average surface temperature while grey error bars reflect the level of variation at the surface. For 67P we include two independent measurements points "A" and "B" as referred to in Tosi et al., (2019) and measured at different heliocentric distances.

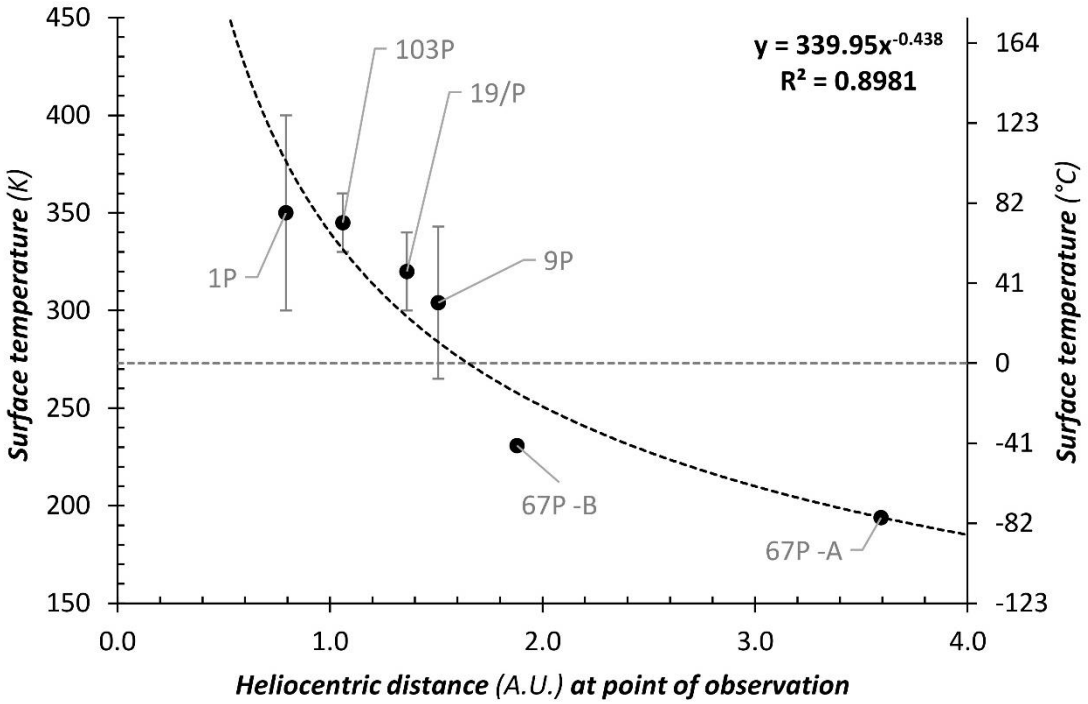

Fig.4. Internal comet subsurface temperatures at perihelion for five periodic comets (1P, 9P, 19P, 67P and 103P), inferred from measured surface temperatures (spacecraft data) and the thermal conduction model of Wickramasinghe et al., (2009). We mark the region at which liquid water may be viable as a shaded blue box, showing that temperatures >0°C could exist down to depths of 40cm on some periodic comets (including 1P, 9P, 19P and 103P).

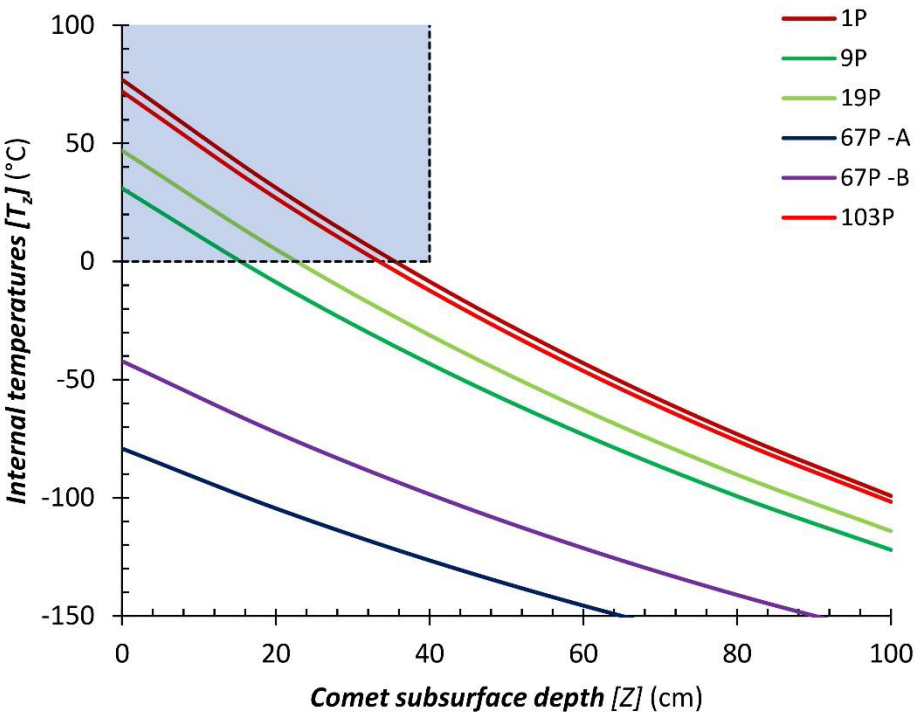

Fig.5. Rotational periods for 37 Jupiter Family comets, varying between 2.8 and 41 hours with a mean average value of 14.4 hours and a median average value of 10.9 hours. Data taken from Kokotanekova et al., (2017).

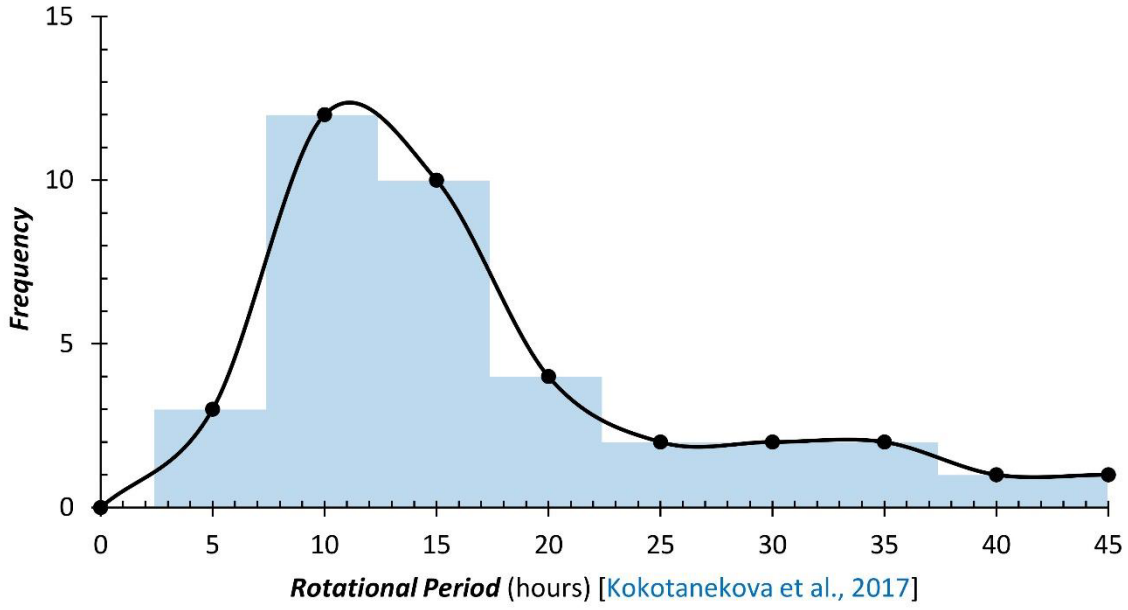

Fig.6. The pressure-temperature phase diagram of pure water-ice showing the stability field for liquid water. Impurities will shift the liquid stability field to lower temperatures (Fig. 2), making liquid water more stable on 9P/Tempel 1. Green lines show the predicted internal temperature (at shallow depths [20cm]) for 5 periodic comets whose surface temperatures have been constrained by spacecraft data. Blue lines plot tensile strength estimates for comets based on spacecraft, meteoroid and modelling data (<270Pa, Greenberg et al., 1995; 20-400Pa, Lisse et al. 1999; <100Pa, Davidsson, 2001; 150Pa Groussin et al., 2013; 1-10kPa, Richardson et al. 2007; 10-80kPa, Trigo-Rodriguez and Blum, 2009 and 700kPa from Spohn et al., 2015).

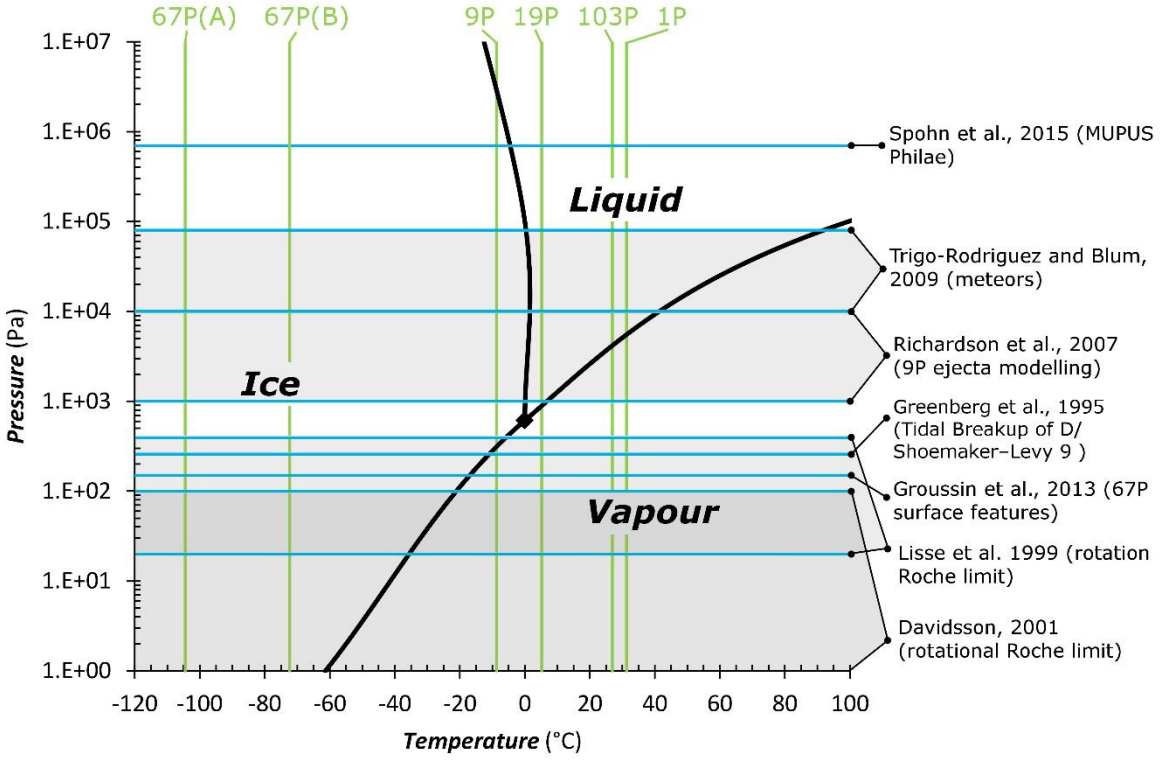

Fig.7. Comparing alteration timescales. This plot shows how long the outermost 10cm of a comet nucleus will survive during a perihelion pass, dependent on the total amount of material shed (between 10-100cm, based on existing literature estimates) and the duration over which this mass loss occurs. The duration over which the outer surface is shed is poorly constrained but appears to be <12 weeks (2016 hours).

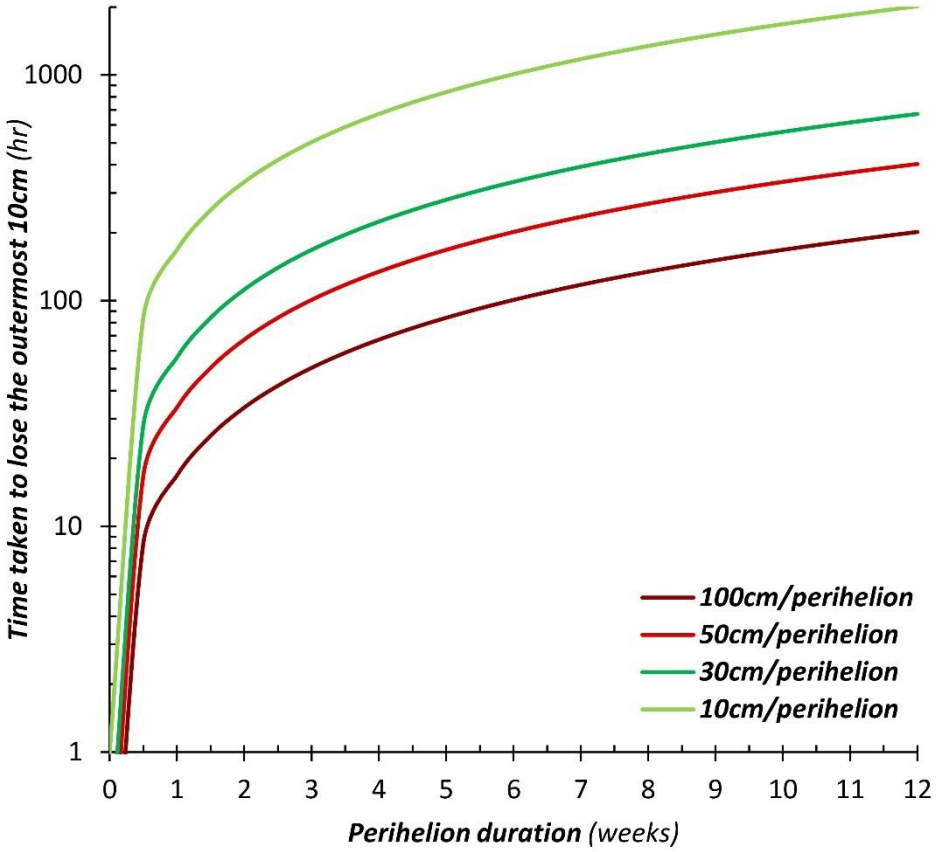

Fig.8. Orbit data (perihelion distance [in A.U.] vs. eccentricity) for 367 known periodic comets. Data taken from the Minor Planet Center (2019). Black and grey bold lines mark perihelion distances of 1.0 and 1.5 A.U. respectively. Ninety-one comets (24.8% of the total) have orbits <1.5 A.U., while 35 comets (9.5% of the total) have orbits <1.0 A.U. Those which pass closest to the Sun during perihelion are most likely to support subsurface liquid water. Blue circles denote comets associated with an active meteor shower reaching Earth today, as described in Jenniskens and Jenniskens (2006) and Jenniskens (2008). The red diamond shows the orbital data for the active asteroid 3200 Phaethon, associated with the late December Geminids meteor shower. Also labelled are 2P/Encke and 96P/Machholz. Note: this plot also shows how small bodies orbits are affected by tidal circularization, reducing their eccentricity.