

## Research Paper

# Evolution of mobile phases in cometary interiors

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### Abstract

Beginning with loose aggregations of dust particles coated with heterogeneous ices under vacuum at Kuiper Belt temperatures, moving to Jupiter/Saturn distances and eventually to low-perihelion orbit, we consider the likely development of the gaseous phase within a cometary nucleus over the course of its lifetime. From the perspective of physical chemistry, we consider limits on the spatial and temporal distribution and composition of this gaseous phase. The implications of the gaseous phase for heat transfer and for the possible spatial and temporal development of liquid phases are calculated. We conclude that the likely temperatures, pressures, and compositions beneath the outer crust of typical cometary nuclei are such that fluidised phases can exist at significant depths and that these reservoirs give a coherent explanation for the high-intensity outbursts observed from cometary nuclei at large distances from perihelion.

**Keywords:** comet – cometary nucleus – cosmochemistry – ices – thermal history

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### 1. Introduction

Jupiter Family Comets (JFCs) are believed to originate proximally in the Kuiper Belt, where temperatures of about 50 K are expected (Emel'yanenko, Asher & Bailey 2013). The subsequent evolution of their internal temperature, and the potential for gaseous and liquid phases of any species to exist in the interior of cometary nuclei, is sensitively dependent on assumptions regarding heat transfer through the predominantly water ice that is presumed to form the continuous phase of a cometary nucleus. Despite a growing awareness of the likelihood of cometary evolution giving rise to subsurface inhomogeneities (Guilbert-Lepoutre et al. 2016), at the present time the consensus view is that cometary interiors are affected very little by events occurring on the surface of the cometary nucleus. This implies the absence of sufficient gas for significant heat or mass transfer within the interior, heating only of a transient ablated layer at the most a few metres in thickness, and no plausible pathway to the generation of significant amounts of liquid (Priyalnik, Benkhoff & Podolak 2004). In this paper, we examine the assumptions behind this consensus and quantitatively assess the probable evolution of gaseous and liquid phases within cometary interiors over the lifetime of a comet.

From observations of short-period comets, it appears likely that many remain in a 'quiescent' state at Jupiter distances, where temperatures of about 110 K are expected, for some time before achieving orbits eccentric enough to become active (Horner, Evans & Bailey 2004). This is consistent with an initial structure of dust grains coated with homogeneous predominantly water ice of mixed composition where volatile species (predominantly CO,

with a triple point temperature of 68.1 K) remain embedded in an unreactive matrix at these temperatures (i.e., either clathrate hydrate structures or amorphous ice with trapped volatile molecules). If the initial structure were heterogeneous ices adhering to dust grains, whether as aggregated small fragments or lamina, observable activity from the sublimation of CO would be expected to be observed at Jupiter distances. Modelling of Centaur objects suggests that a typical object at an average orbital position of 5.5 AU will have a half-life of order  $10^6$  yr (Horner et al. 2004). Thus, it is reasonable to assume that a typical JFC will have spent a time of order  $10^6$  yr under conditions where thermal equilibrium corresponds to a temperature of about 110 K before it experiences temperatures sufficient to disrupt the ice matrix at any point in its volume.

Much current modelling of cometary nuclei has suggested that heat transfer through the interior is slow enough that surface layers are ablated on approach to the sun while the interior remains at Kuiper Belt temperatures and can be considered as a 'pristine' relic of the early solar system (e.g., Priyalnik et al. 2004: Figure 6, p. 377). Conversely, other bodies have been identified as 'ex-comets' which have been depleted of volatiles and are no longer active, for example, (4015) Wilson Harrington (Guilbert-Lepoutre et al. 2015). These two postulates cannot be simultaneously true given that comets are quiescent at Jupiter distances: for a comet to be 'depleted of volatiles', its entire interior must have been warmed at one time to a level sufficient for sublimation of the predominantly water ice matrix in order for volatile species to escape. Depending on the initial assumptions made about the nature of the cometary interior, this means at a minimum the temperature for the phase transition from amorphous to crystalline ice (approximately 90 K) (Schmitt et al. 1989). Alternatively, the surface must have been processed enough to produce an impermeable layer, again incompatible with ablation of a pristine core.

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**Table 1.** Temperatures for persistence of gas. Note that a literature value for heat of sublimation of oxygen could not be found so the calculation was carried out for a range of plausible values for  $B$ .

	$P_{tr}$ (Pa)	$T_{tr}$ (K)	$B$ (K)	$d$ (pm)	$T$ (K)	
					1 cm pores	100 $\mu$ m pores
CO	$1.537 \times 10^4$	68.1	764.16	376	33	41
CO <sub>2</sub>	$5.17 \times 10^5$	216.55	2148	330	110	131
O <sub>2</sub>	146	54.36	1110	346	40	49
N <sub>2</sub>	$1.252 \times 10^4$	63.151	830	364	34	41
CH <sub>4</sub>	$1.17 \times 10^4$	90.98	1190.2	380	49	60

Kinetic diameters,  $d$ , are taken from Matteucci *et al.* (2006) and Mehio, Dai & Jiang (2014).

The internal temperature of a comet when it begins to experience a thermal flux significant enough to degrade surface ices is the key variable for understanding the internal evolution of cometary nuclei. If this internal temperature remains below the sublimation point of CO, the internal pores of the nucleus will remain unoccupied by gas. If the internal temperature is above this point, the interior will be occupied by a gas phase. This phase will arise from the fact that gaseous molecules subliming into vacuum from a surface layer, even on the order of  $10^{-3}$  m thickness, will find an isotropic environment; initially, they will have an equal probability of diffusing from the surface layer either out of or into the cometary nucleus. Once this vacuum is occupied, the internal gas phase will be maintained by the rate of diffusion outward, which will be significantly slower as the rate of diffusion through a gas will be lower than the rate of diffusion through a vacuum. To our knowledge, the possible development of this internal gas phase has not been considered in the previous work, which has assumed the partial gas pressure to be equal to the saturation pressure wherever a species can condense out (e.g., Marboeuf *et al.* 2012). Any internal gas phase will contribute an advective component to heating of the interior, which under some plausible sets of conditions may be more significant than convective heating of the cometary core (Prialdnik 1992). Besides CO, a species that has recently been found in comparable levels to CO in the coma of 67P/Churyumov-Gerasimenko is molecular oxygen (Bieler *et al.* 2015), while smaller amounts of methane (Gibb *et al.* 2003) and nitrogen (Rubin *et al.*, 2015) have also been observed in some cometary comae, and these four species are all likely candidates for persisting in the gaseous state in the cold interior of comets.

## 2. Possible gaseous species under Kuiper Belt and Jupiter orbit conditions

The sublimation temperature for any gas is below its triple point temperature,  $T_{tr}$ , and can be estimated using the Clausius–Clapeyron relation for determining the vapour pressure,  $P$ , at any temperature:

$$P = P_{tr} \exp \left( B \left( \frac{1}{T_{tr}} - \frac{1}{T} \right) \right), \quad (1)$$

where  $P_{tr}$  is the triple point pressure and  $B$  is approximately the molar heat of sublimation divided by the product of  $k_B$ , Boltzmann's constant, and  $N_A$ , Avogadro's number. Sublimation will be possible when the temperature is such that  $P$  is above the effective pressure caused by collisions with the walls of the pores in the cometary interior:

$$P_{eff} = \frac{k_B T}{\sqrt{2\pi} d^2 l}, \quad (2)$$

where the average pathlength between collisions,  $l$ , is equal to the diameter of the pores in the comet interior and  $d$  is the kinetic diameter of the gas-phase molecules.

In Table 1, values for triple point pressure and temperature and the parameter  $B$  and molecular diameter are given for CO, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub> along with the temperature at which  $P = P_{eff}$  for average pore sizes of 1 cm and 100  $\mu$ m.

It appears likely from the calculations above that cometary nuclei resident in the Kuiper Belt where temperatures are typically of order 50 K will be at least warm enough for any CO, O<sub>2</sub> or N<sub>2</sub> to remain in the gas phase throughout the interior, once these molecules are liberated from the ice matrix. The persistence of methane is also probable, depending on the interior pore size distribution. The fact that considerable amounts of these hypervolatile species are observed in cometary outbursts is strong evidence for the postulated speciation of these species as components of a 'dirty ice' matrix, rather than existing in separate phases of a heterogeneous ice: over billions of years at Kuiper Belt temperatures, any of these species existing in separate domains exposed to vacuum would have sublimed and diffused from the cometary interior (Miles 2016; Gronkowski & Sacharczuk 2010).

As far as the possibility of any significant fraction of CO<sub>2</sub> remaining in the gas phase once liberated from the ice matrix, the next question to be addressed becomes: is the typical time spent by a pre-active cometary nucleus at distances corresponding to Jupiter or Saturn orbital distances sufficient for the interior of the comet to reach thermal equilibrium?

## 3. Parameters for heat transfer in cometary nuclei

A characteristic time for heat transfer through a sphere can be defined as (Prialdnik *et al.* 2004):

$$t = \frac{R^2 \rho c_p}{\pi^2 k}, \quad (3)$$

where  $R$  is radial distance and  $\rho$ ,  $c_p$ , and  $k$  are respectively the density, heat capacity, and thermal conductivity of the material. For pure H<sub>2</sub>O ice, the behaviour of the heat capacity and thermal conductivity with temperature is well understood. The value of  $c_p$  can be determined by extrapolating down from experimental values (1389 J kg<sup>-1</sup> K<sup>-1</sup> at 173 K) along the curve of the Debye relation (Horner *et al.* 2004)

$$c_p = 9k_B N_A \left( \frac{T}{T_D} \right)^3 \int_0^{T_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx, \quad (4)$$

**Table 2.** Characteristic time (years) for thermal equilibrium of a cometary nucleus.

T (K)	High limit porosity correction ( $\phi = 0.4$ )			Low limit porosity correction ( $\phi = 4 \times 10^{-5}$ )		
	R = 1000 m	2000 m	5000 m	R = 1000 m	2000 m	5000 m
180	3 300	13 000	83 000	$3.3 \times 10^7$	$1.3 \times 10^8$	$8.3 \times 10^8$
150	2 700	11 000	67 000	$2.7 \times 10^7$	$1.0 \times 10^8$	$6.7 \times 10^8$
120	1 900	7 600	48 000	$1.9 \times 10^7$	$7.6 \times 10^7$	$4.8 \times 10^8$
110	1 700	6 700	42 000	$1.7 \times 10^7$	$6.7 \times 10^7$	$4.2 \times 10^8$
100	1 400	5 700	36 000	$1.4 \times 10^7$	$5.7 \times 10^7$	$3.6 \times 10^8$
90	1 200	4 800	30 000	$1.2 \times 10^7$	$4.8 \times 10^7$	$3.0 \times 10^8$
80	930	3 700	23 000	$9.3 \times 10^6$	$3.7 \times 10^7$	$2.3 \times 10^8$
70	700	2 800	18 000	$7.0 \times 10^6$	$2.8 \times 10^7$	$1.8 \times 10^8$
60	510	2 100	13 000	$5.1 \times 10^6$	$2.1 \times 10^7$	$1.3 \times 10^8$
50	260	1 000	6 400	$2.6 \times 10^6$	$1.0 \times 10^7$	$6.4 \times 10^7$

where  $T_D = 300$  K is the Debye temperature of ice at 100K (Flubacher, Leadbetter & Morrison 1970).

Thermal conductivity is given by the empirical relation,  $k = 567/T$  ( $\text{Wm}^{-1} \text{K}^{-1}$ ) (Prialnik et al. 2004) which provides a good fit to experimental data between 20 and 200 K (Klinger 1975).

Characteristic heat transfer times calculated by Equation (3) will give an absolute upper limit to the heating rate of a cometary interior for three reasons: (1) porosity, (2) the possibility of amorphous rather than crystalline water ice, and (3) reduced heat conductivity of clathrates.

### 3.1. Porosity ( $\psi$ )

The overall density of cometary nuclei is such that their interiors cannot be solid but must contain a substantial fraction (approximately 50%,  $\psi = 0.5$ ) of voids. Prialnik et al. (2004) review a number of models for estimating the effect of voids on thermal conductivity, which show a maximum divergence (approximately 4.5 orders of magnitude) for the porosity correction factor  $\phi$  at  $\psi = 0.5$ . At the high end of the range of correction factors, the Maxwell relation

$$\phi = \frac{(2 - 2\psi) + (1 + 2\psi)k_p/k_s}{(2 + \psi) + (1 - \psi)k_p/k_s}, \tag{5}$$

where  $k_s$  is the thermal conductivity of the ice grains and  $k_p$  is the thermal conductivity of the voids (Smoluchowski 1982), gives a value of  $\phi = 0.4$  at a  $k_p/k_s$  ratio of  $10^{-5}$ . This is of similar magnitude to the value of 0.14 predicted by the empirical relation [ $\phi = (1 - \psi)/(1 + 10\psi^2)$ ] (Koh & Fortini 1971) found to hold for a range of sintered powder materials, the results of Monte Carlo simulations (Shoshany, Prialnik & Podolak 2002), and experimental values for heat transfer in snow cf. solid ice (Bartels-Rausch et al. 2013). Values in this high-end range are plausible so long as the interior of the comet nucleus can be described as sintered ice-covered dust grains. It would seem that  $k_p$  ought necessarily to be 0 as the thermal conductivity of a vacuum. However,  $k_p$  is radiative flux, which may be estimated by  $4\epsilon\sigma rT^3$ , where  $\epsilon$  is the emissivity coefficient (approximately 1 for water ice),  $\sigma$  is the Stefan-Boltzmann constant, and  $r$  is the radius of the pores (Prialnik et al. 2004). Clearly, this value will be sensitively dependent on the (unknown) average dimension of the voids within a cometary nucleus: at Kuiper Belt temperatures (50 K),  $k_p/k_s$  will

be  $10^{-5}$  at a pore radius of 400  $\mu\text{m}$  and less for smaller pores; at Jupiter temperatures (110 K),  $k_p/k_s$  will be  $10^{-5}$  at a pore radius of 40  $\mu\text{m}$  and less for smaller pores. It should also be noted that the Stefan-Boltzmann law is no longer applicable when the pore size is comparable to the characteristic wavelength of thermal radiation (approximately 60 microns at 50 K and 25 microns at 110 K), below which radiative flux becomes greater than predicted by this relation, so this  $k_p/k_s$  ratio of  $10^{-5}$  is close to the theoretical extreme minimum (Lim et al. 2015).

At the low end of the range, a value of  $\phi$  may be estimated using an inversion of the Maxwell relation (i.e., ice particles dispersed in a matrix of vacuum rather than vice versa) (Prialnik et al. 2004).

$$\phi = \frac{k_p(3 - 2\psi) + 2\psi k_p/k_s}{k_s\psi + (3 - \psi)k_p/k_s}. \tag{6}$$

A  $k_p/k_s$  ratio of  $10^{-5}$  gives a value of  $\phi = 4 \times 10^{-5}$ .

In Table 2, a characteristic time for thermal equilibrium (years) is estimated using Equation 3 following Prialnik et al. (2004) at differing fractions of the Debye temperature  $T_D$  for water ice corresponding to temperatures between Kuiper Belt (50 K) and Jupiter orbit values (110–120 K), using an estimated ice density of  $925 \text{ kg m}^{-3}$ . Times for thermal equilibrium at typical thermodynamic equilibrium temperatures for JFC in active orbits (150–180 K) are also shown. Note that the low limit porosity correction values imply that the lifetime of the solar system is sufficient for all Kuiper Belt bodies of cometary size to reach thermal equilibrium.

It can be seen that for a sintered matrix ( $\phi = 0.4$ ), typical estimated residence times at Jupiter/Saturn distances of order  $10^5$  yr should be sufficient for the interior to reach thermal equilibrium for a range of plausible cometary dimensions. On the contrary, for a loose matrix ( $\phi = 4 \times 10^{-5}$ ) these typical residence times are always insufficient by at least an order of magnitude. Modelling suggests that colliding dust particles under cometary formation conditions will have a minimal contact area (of order of a billionth of their surface area) (Skorov & Blum 2012), which is not well described as a sintered matrix. However, under high vacuum surfaces in contact with each other typically become sintered together, a process which will be controlled by the average lifetime of a molecule on a surface,  $\tau$  (Somorjai 1994).

**Table 3.** Residence times of water molecules on surface as a function of temperature for  $\tau_0 = 10^{-13}$  s. Enthalpy of sublimation values from Feistel and Wagner (2007).

$T$ (K)	$\tau$ (yr)
180	$1.8 \times 10^{-6}$
150	$1.3 \times 10^{-3}$
120	23
110	$1.8 \times 10^3$
100	$3.6 \times 10^5$
90	$2.2 \times 10^8$
80	$6.6 \times 10^{11}$
70	$1.9 \times 10^{16}$

$$\tau = \tau_0 \exp\left(\frac{-\Delta H_{\text{sub}}}{k_B N_A T}\right), \quad (7)$$

where  $\tau_0$  is the time of the surface bond vibration, or 1/frequency of the surface bond vibrational frequency and  $\Delta H_{\text{sub}}$  is the enthalpy of sublimation.

The data in Table 3 suggest that the timescale for the migration of surface water molecules from high-energy to low-energy sites, which will act to reduce the area of the vacuum/grain interface and seal microcracks, is plausible at the temperatures experienced at the surface of JFC at Jupiter–Saturn distances. Thus, it is reasonable that it is at this temperature range (110–120 K) that an initially loosely aggregated cometary nucleus will transition to a sintered matrix and transfer from the low limit porosity correction to the high limit porosity correction regime.

### 3.2. Amorphous versus crystalline ice

According to the Nice model (Gomes *et al.* 2005), planetesimals were formed at a range of 20–40 AU and thrown outwards to become comets. At the temperatures (approximately 30–40 K) and pressures ( $1.3 \times 10^{-5} - 1.7 \times 10^{-4}$  Pa) postulated in the early solar system at 20–40 AU, water would be expected to be deposited as amorphous ice (Willacy *et al.* 2015). (Kouchi *et al.* 1992) have demonstrated extremely low-thermal conductivity for amorphous ice formed by vapour deposition, of order of  $10^{-4}$ – $10^{-5}$  times lower than crystalline ice at a temperature of about 120 K. Applying a correction factor of this order to the times given in Table 2 will clearly give times much longer than the residence time of comets at Jupiter/Saturn distances.

However, Kouchi *et al.* (1992) found that amorphous ice formed only in layers up to 60  $\mu\text{m}$  thick, and that further deposition gave crystalline ice; furthermore, amorphous ice formed by compression, rather than vapour deposition, has been found to have thermal properties not dissimilar to crystalline ice ( $k = 0.6 \text{ W m}^{-1} \text{ K}^{-1}$ ) (Andersson & Suga 1994).

Experimentally, the D/H ratio observed in cometary water suggests that they have been exposed to higher temperature conditions and should be composed of crystalline ice.<sup>a</sup> The outgassing

<sup>a</sup>Willacy *et al.* (2015) state: ‘Regardless the possible presence of clathrates, there is today indirect evidence that comets formed from crystalline water ice because their deuterium-to-hydrogen ratios measured in  $\text{H}_2\text{O}$  are substantially lower ( $\sim 6$ – $12$  times the protosolar value) than the most deuterium-rich primitive meteorite ( $\sim 35$  times the protosolar value), whose level of deuteration is expected to be close to the one found in the ice infalling

pattern observed from comet 67P/Churyumov-Gerasimenko has been reported to be more consistent with crystalline ice containing volatile gases in clathrates than amorphous ice (Luspay-Kuti *et al.* 2016). Furthermore, spectroscopic observations of Kuiper Belt bodies are also consistent with crystalline, rather than amorphous ice, albeit these are larger bodies which may have been heated by internal radiation (Jewitt & Luu 2005; Delsanti *et al.* 2011; Brown & Calvin 2000).

### 3.3 Clathrate conductivity

A strong caveat to any discussion of the heat transport properties of the matrix material of cometary nuclei is that while predominantly water, it is likely to be (considering the circumstances of its formation, and as we have asserted at the outset based on evidence of cometary behaviour at Jupiter distances) either a clathrate or a solid solution containing significant quantities of other ice-phase materials observed in comets: predominantly  $\text{CO}_2$ , but also CO, and methanol. The thermal properties of these materials are not well known, though for methane hydrate the data of Krivchikov *et al.* (2005) suggest values approximately an order of magnitude less than those of water over the temperature range of interest.

Thus, it is evident that heat transfer in cometary nuclei will be largely controlled by assumptions not currently amenable to direct experimental observation. If the interior is composed of disaggregated grains, or of a continuous network with the properties observed for thin layers of amorphous ice by Kouchi *et al.* (1992), then heating of the interior will have been very limited and it can be considered as primeval. If the interior is composed of grains where ice exists in the form that has hitherto been observed in Kuiper Belt objects and has been exposed to temperatures of order 110–120 K for of order  $10^3$ – $10^4$  yr, then conservative estimates for conductive heating of cometary nuclei suggest that almost all objects for which we observe activity will have had sufficient time before becoming active to reach thermal equilibrium at Jupiter–Saturn distances, as the amorphous to crystalline phase transition and sintering of grains progresses inward at temperatures under conditions where there is negligible ablation. This will give an interior temperature that is everywhere well above the sublimation temperatures of CO,  $\text{O}_2$ , and methane.

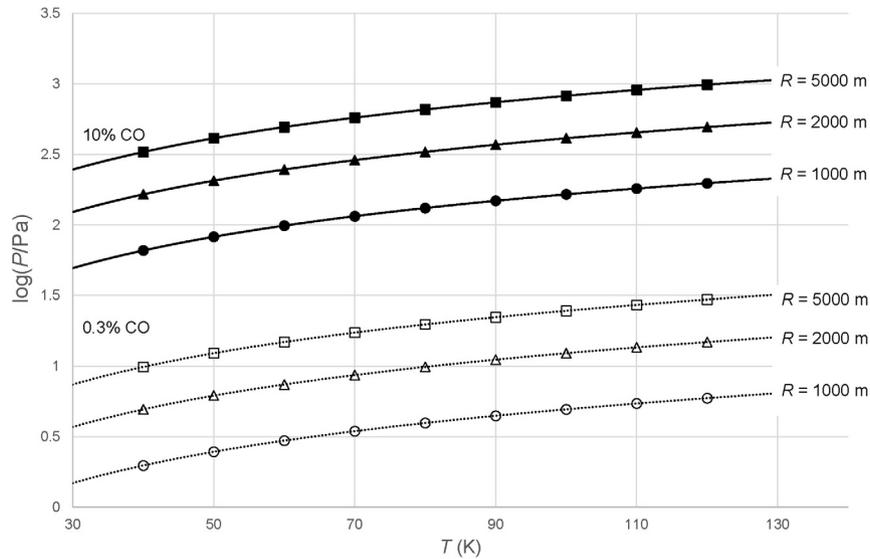
These calculations also suggest that at least some cometary nuclei that have been resident in Jupiter-distance orbits will have an interior temperature sufficient for  $\text{CO}_2$  to remain in the gaseous state once released; this possible case will not be considered in the discussion below, which will address only the formation of an internal atmosphere from the more volatile species.

It should be noted that it is clearly not necessary for this initial heating to occur for an internal gaseous phase to be generated once the surface of a cometary nucleus warms, as a consequence of the low sublimation pressure of CO,  $\text{O}_2$ , and  $\text{CH}_4$  (Table 1).

## 4. Initial internal atmosphere

On initial approach to the sun, at a surface temperature of approximately 180 K, sublimation of exposed water ice will become

from the presolar disk. This difference can only be explained by the isotopic exchange between the deuterium-rich water and molecular hydrogen in the gas phase. Hence, in order to enable this reaction, amorphous ice entering the disk from ISM must have been vaporised prior to recondensing again in crystalline form, otherwise the isotopic exchange did not occur’ (Lim *et al.* 2015; Andersson & Suga 1994).



**Figure 1.** Limiting internal pressures from surface carbon monoxide sublimation for cometary ices composed of 10 and 0.3% CO.

significant (of order 1 mg per square metre per second) (Andreas 2007). As this ice sublimates, we postulate that more volatile components within the predominantly water matrix will also be released, and the gas generated will diffuse in an undifferentiated fashion both away from the surface of the nucleus and inward into an initially empty interior Küomle et al., (1991), leaving a porous surface layer of dust grains and ice depleted in volatiles (Poch et al. 2016a, 2016b). This layer will arise because water and methanol, with a sublimation point significantly above the internal temperature of the nucleus, will recondense rapidly at no great distance from where they were generated. Carbon dioxide is also likely to recondense, having diffused a greater distance before doing so, giving a physical basis for the patches of differentiated water and CO<sub>2</sub> ice observed on ablation of the surface of comet 67P/Churyumov-Gerasimenko (Filacchione et al. 2016; Pommerol et al. 2015).

However, carbon monoxide and the less frequently observed components oxygen, nitrogen, and methane will not recondense at the internal temperatures likely to be prevailing in the interior of the comet. The calculation below will estimate initial internal pressure based on the conservative case where only CO contributes to the formation of this phase.

Estimates of CO content of cometary ices range between 0.3 and 30% relative to water Mumma & Charnley (2011). Indeed, gas production levels of CO of a similar magnitude to water have been observed in cometary outbursts (Kawakita et al. 2014). Assuming an initial erosion of about a 2-m layer over the surface of a comet over the course of a perihelion event, composed of 50% pores and with an ice/dust ratio of 1:1, would give a mass of CO sufficient to provide an appreciable internal gaseous phase to a comet.

In Figure 1, the resulting final internal pressures in Pa if 10% of the CO generated was to diffuse into the interior of the comet, assuming ideal gas behaviour, are given.

These figures are likely to be misleading due to the slow rate of gas diffusion into a homogeneously porous cometary interior. The diffusion coefficient scales with temperature and pressure according to the expression (Cussler 1997):

$$D \propto \frac{T^{1.5}}{P}. \quad (8)$$

And a characteristic time for diffusion, a given distance  $s$  can be estimated using the expression for root-mean-square diffusion in three dimensions

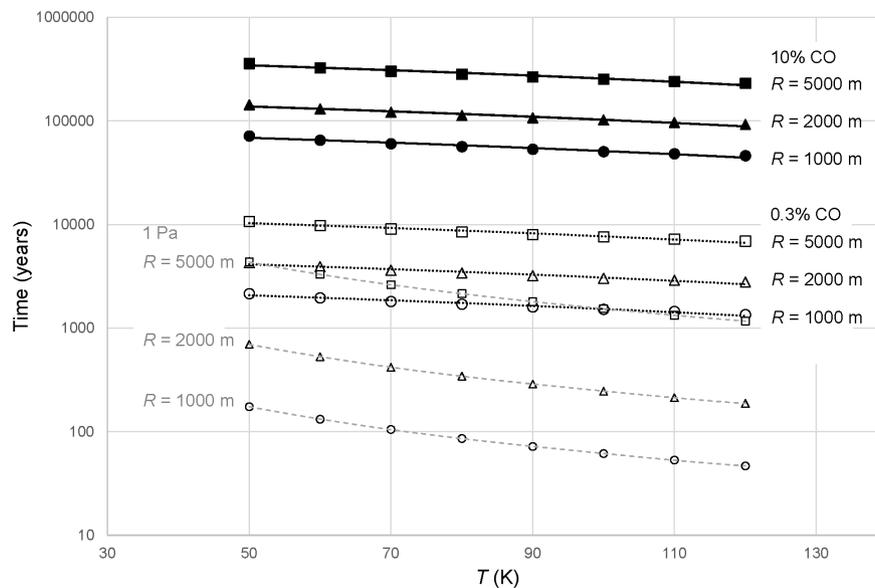
$$s^2 = 6Dt. \quad (9)$$

The timescale for diffusion of small molecules into the comet interior in years was estimated assuming a similar effective diffusion coefficient as for methanol in dry snow at 243 K and 10<sup>5</sup> Pa ( $D = 8.0 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$ ) (Bartels-Rausch et al. 2013), then scaled according to Equation (7). These are shown in Figure 2, along with the comparable times for diffusion of a dilute CO gas against the effective interior pressure  $P_{\text{eff}}$  calculated for a pore size of 300  $\mu\text{m}$ . Gravitational and rotational forces on the diffusing molecules will be many orders of magnitude less than thermal ones and can be neglected.

#### 4.1 Persistence of an internal atmosphere

The values in Figure 2 suggest that after a relatively short time the interior of a cometary nucleus will fill with gas, such that the effective sublimation pressure  $P_{\text{eff}}$  due to the dimensions of the pores is exceeded throughout. Degassing of this atmosphere should take up to an order of magnitude longer than the initial filling period even in the absence of any structural changes on the surface to retard diffusion. These values suggest that there is little chance that a JFC will lose all the internal volatiles generated by a single initial perihelion event during the period before its next approach to the sun. A comet nucleus ‘depleted of volatiles’ must arise through more violent processes. Clearly, these first rough estimates demonstrate that the estimation of the actual internal pressure immediately below the surface requires a far more complex and dynamic approach than has been attempted here; even the small amount of CO gas generated from ablation of a 2-m depth surface is likely to give rise to localised internal pressures significantly above those estimated in Figure 1.

The re-freezing of sublimed water and carbon dioxide diffusing into the interior of the nucleus will generate a layer of significantly lower permeability that will prevent internal gas from rapidly exiting the nucleus. In addition, it should be noted that the initial



**Figure 2.** Characteristic times for diffusion of small molecules through empty comet nuclei interiors and comet nuclei containing atmospheres of carbon monoxide as per Figure 1.

diffusion into an empty interior will be many orders of magnitude more rapid than later diffusion outwards against a significant pressure. Thus, once established, an internal atmosphere can be expected to remain extant throughout the subsequent lifetime of the comet.

Within broad uncertainties, the values in Figure 1 can therefore be considered plausible minimum pressures for the interior environment near the surface of a cometary nucleus at times near perihelion. The caveat must be made that the degree of heterogeneity of the cometary interior is unknown and it may be possible that there are connected channels of larger dimensions which would allow much more rapid gas transport, which would clearly impact on both the initial filling of the comet and its subsequent outgassing.

## 5. Consequences of an internal atmosphere

### 5.1 Advective heating

The first consequence of an internal atmosphere will be more rapid heat transfer to the interior of the comet, as advective heating becomes possible. A lower limit to the degree of advective heating can be estimated by taking the core pressure achievable in a typical cometary lifetime of 12 000 yr and attributing this pressure to material initially generated at a lower sublimation limit of 180 K. It is reasonable to assume that material exposed to higher temperatures will preferentially be lost from the comet.

Heat transfer to the core may then be estimated by equating:

$$-m(\text{CO})c_p(\text{CO})\Delta T(\text{CO}) = -m(\text{matrix})c_p(\text{matrix})\Delta T(\text{matrix}) \quad (10)$$

for a  $1 \text{ m}^3$  element of matrix. The specific heat of CO was estimated at  $1039 \text{ JK}^{-1} \text{ kg}^{-1}$  and the specific heat of the matrix estimated to be  $350 \text{ JK}^{-1} \text{ kg}^{-1}$  at 50 K and  $1200 \text{ JK}^{-1} \text{ kg}^{-1}$  at 120 K, while the mass of the matrix per  $\text{m}^3$  was estimated to be 500 kg.

Heat transfer achievable in 12 000 yr through diffusion against the limiting pressure was estimated using Equations (4), (5),

**Table 4.** Advective heating of cometary interiors.

$R$ (m)	CO (%)	$T$ core (K)	$\Delta T$ (K)
Diffusion-limited			
5 000	0.3	120	$6.7 \times 10^{-4}$
1 000	10	50	$8.0 \times 10^{-2}$
Full transfer			
5 000	0.3	50	$6.9 \times 10^{-2}$
		120	$9.4 \times 10^{-3}$
1 000	10	50	2.3
		120	0.31
	0.3	50	0.34
		120	$4.6 \times 10^{-2}$
10	50	12	
	120	1.6	

and (8) for the cases of  $R = 1000 \text{ m}$ ,  $T = 50 \text{ K}$ , 10% CO and  $R = 5000 \text{ m}$ ,  $T = 120 \text{ K}$ , 0.3% CO. These are shown in Table 4, together with the temperature increase in the matrix attributable to heat transfer from the gas. For the alternative limiting case, where there is sufficient fracturing for the gas generated to fill the core entirely over the course of one perihelion pass, the temperature increase brought about by heat transfer over a postulated lifetime of 500 orbits is given.

These calculations suggest that the contribution of advective heating to warming comet interiors will be minimal, unless a much larger proportion of gas generated on subsequent approaches to the sun than the 10% estimated here flows into the interior of the nucleus and that this transfer occurs more rapidly than diffusion. Only under these conditions, may it be possible for poorly conductive comet interiors to approach their thermodynamic equilibrium temperature by solar heating over a typical active lifetime, as was

estimated by a previous generation of researchers (Herman & Weissman 1987).

## 5.2 Liquid phases

While water and carbon dioxide will remain solid at the thermodynamic equilibrium temperature of cometary nuclei, and so deep in the interior the porosity of the ice phase and its homogeneous composition will be maintained, there are species present in reasonable quantities which may form liquid phases throughout a cometary interior, as previously discussed by others (Miles & Faillace 2012)—note the triple points in Figure 3(a).

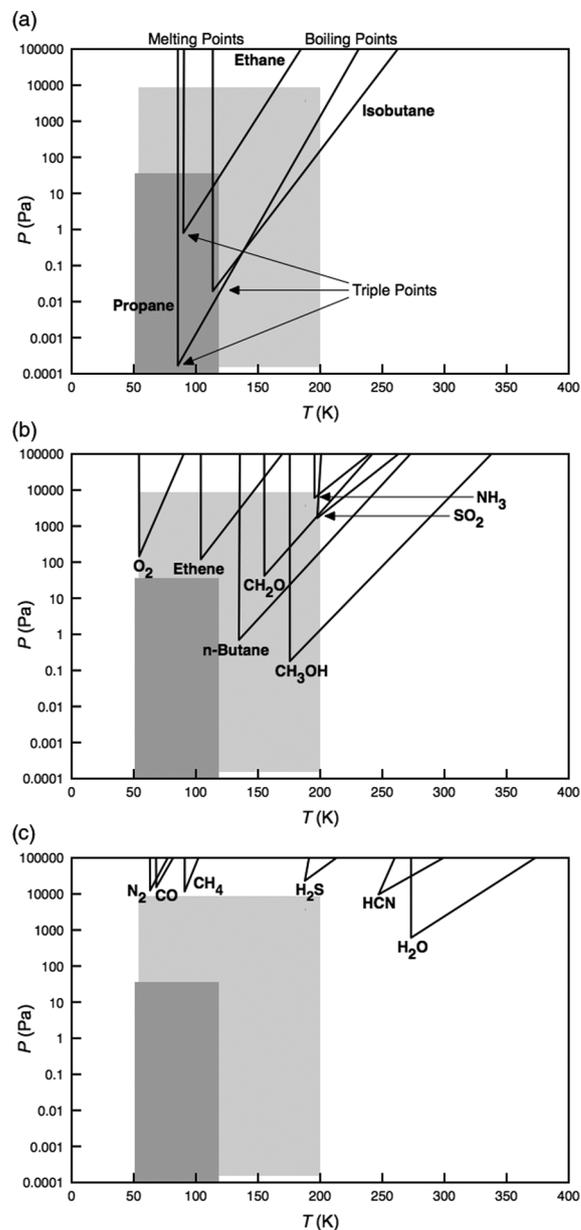
Both ethane and methanol have been reported at significant concentration in cometary atmospheres (approximately 1% of water) and are credible as components of a liquid phase condensing from a disrupted matrix (Le Roy et al. 2015). Propane and butane have been credibly observed in the coma of 67P/Churyumov-Gerasimenko, though at relatively low concentrations (Altwegg et al. 2017); under conditions readily realisable at JFC distances, these species will be liquid under a wide range of temperatures and pressures. While methanol has a triple point at the high end of the equilibrium temperatures credible for JFC ( $T_{tr} = 175.6$  K,  $P_{tr} = 0.18$  Pa), this is a temperature that will frequently be encountered at the surface of cometary nuclei. Note that this pressure is far lower than any of the pressures considered above, suggesting that wherever the comet interior is warmed above 175.6 K it will be possible to find liquid methanol.

## 5.3 Subsurface fractionation

A primary consequence of the process which could initially generate an internal cometary atmosphere by sublimation and dispersal of a surface layer will be the variety of fractionation processes and ensuing chemical differentiation possible in the immediate subsurface volume. As an impermeable outer layer is generated, the differing sublimation temperatures of carbon dioxide and water will lead to a degree of fractionation: the low-porosity solid layer will not be composed of a solid solution of 'dirty water' ice, but is likely to contain zones of purer water ice on the outside and deposits of carbon dioxide and methanol ice in the interior. The observed presence of surface patches of concentrated carbon dioxide ice are only plausible if there are significant reservoirs of carbon dioxide concentrated below the surface which freeze on encountering night-side temperatures, that is, they are not compatible with ablation of a homogeneous low temperature core (Capria et al. 2017).

On the second perihelion of the comet, therefore, it is likely that the immediate subsurface will be warmed enough to sublime carbon dioxide (approximately  $>150$  K at 1 000 Pa) at temperatures too low to disrupt the outer layer of water ice (approximately  $<180$  K). This will lead to an increase in pressure in the immediate subsurface region which should easily reach of order  $10^4$  Pa, supplying sufficient internal pressure to account for the significant eruptive events observed from cometary surfaces.

In addition, such a temperature would see the generation of a liquid methanol phase which in the aftermath of eruptive events will act as a rapidly evaporating methanol-based slurry that will bring concentrations of higher organics, soluble in methanol, to the surface. Given the variety of organic species known to be present in cometary nuclei, much scope exists for the fractionation and differentiation of materials in the cometary subsurface (Miles 2016; Rubin et al. 2019).



**Figure 3.** Triple points of volatile species observed in comets, mapping the rough range over which they will be liquid. The grey rectangles correspond to conditions plausible within the entire interior of a cometary nucleus on initial formation of an atmosphere (darkest rectangle), with liquid phases possible under these conditions shown in (a), and upon attainment of thermodynamic equilibrium (lightest rectangle), with liquid phases possible under these conditions shown in (b). Higher pressures and temperatures will be possible only in limited volumes and durations within a cometary nucleus, potentially giving rise to further liquid phases (c).

Heating of the interior to temperatures high enough to support liquid water will obviously not be possible so long as pressurisation is provided solely by an external layer of non-porous water ice. As a comet continues to lose ice from the surface, however, the surface will increasingly come to consist of ice-free dust particles and concentrated higher organics photopolymerised into an intractable matrix (Wilson & Sagan 1997; Matthews & Minard 2006; Simonia 2011). Silicates have a thermal conductivity that is likely to be of order  $1 \text{ W m}^{-1} \text{ K}^{-1}$ , an order of magnitude greater than the ice conductivities used in these estimates, with a heat capacity that is likely to be somewhat lower than ice (Robinson & Haas 1983). It

will clearly be possible to heat this refractory material to temperatures well above the triple point temperature of water (273.16 K) and such temperatures have frequently been reported for cometary surfaces (Groussin *et al.* 2006; Emerich *et al.* 1987). Beneath such a layer, only the relatively low triple point pressure of water (611 Pa) will be required. Sufficient pressure could be generated from CO alone for liquid water to exist, but the abundance of CO<sub>2</sub> likely to form transient gas phases beneath the warming surface means pressures considerably above this are possible.

The previous cycles of fractionation and densification will make the porosity-derived assumptions of very slow heating untenable within the modified zone, and estimations of the timescale of heating readily show that a liquid/mud layer of order of metres in thickness can form over the course of a perihelion event. Only the permeability and cohesive strength of the outer refractory layer will limit the pressure achievable beneath the surface, and only the incident solar flux will limit the temperatures achievable; for example, surface temperatures at the equator of order 400 K have been estimated for near-Earth asteroids such as (162173) Ryugu (Busareva *et al.* 2018). Eventual rupture of the cemented dust layer to release a water-based slurry can account for the mud-bath-like features attributed to flow of fluidised material observed in association with ruptures on cometary surfaces (Thomas *et al.* 2015), structures consistent with conduits for liquid flow (Auger *et al.* 2015), and for the very high-volume eruptions observed in some comets at considerable distances from the sun (Gronkowski & Wesołowski 2016; West, Hainaut & Smette 1991). For example, observation of the post-perihelion eruption of 67P/Churyumov-Gerasimenko at a distance of 3.32 AU has indicated that there must be a mechanism for significant energy storage well beneath the surface of the cometary nucleus (Agarwal *et al.* 2017).

The plausibility of these high temperatures and liquid water in such upper volumes of the comet can also explain the existence of minerals observed on comet 81P/Wild2 which could only be formed under aqueous conditions (Berger *et al.* 2011).

All these features are incompatible with cometary nuclei at thermal equilibrium with their surroundings, but arise naturally given the low rates of heat and mass transport into the interior which we have discussed. These are not the extraordinarily low rates based on the properties of amorphous water ice with very high porosity, which may be applicable at temperatures of a few tens of K, but the rates plausible once the surface is exposed to temperatures JFCs will experience for times of order 10<sup>3</sup> yr, sufficient for grain sintering and for any amorphous/crystalline phase transition to propagate inwards from the surface. It is these low transfer rates that allow subsurface heating above the thermodynamic equilibrium temperature of the comet, to levels transiently sufficient for the existence of liquids and complex fractionation processes.

Finally, it should be noted that the postulated sequence of events outlined does make it possible for a comet to ‘exhaust all its volatiles’, not by losing all of the volatile species in the comet, but by building up over successive approaches to the sun an outer layer of cemented dust which is thick enough so that incident heat can no longer melt the subsurface layers of water or carbon dioxide ice over the course of a perihelion event.

## 6. Non-solar heating

In the areas of high pressure beneath the postulated low-porosity skin, the possible existence of liquids will make possible other

sources of heating through exothermic reactions of liquid water with other constituents of the comet. Heat of solution on dissolution of CO and CO<sub>2</sub> in liquid phases of hydrocarbons and methanol as a source of heating may provide a significant mechanism for the transfer of thermal energy and heat storage at depth (Miles 2016). Also of possible significance is the heat released on formation of mixed methanol/water phases when gaseous methanol condenses to ‘pre-melt’ water ice (Miles 2016). Under the transient conditions where aqueous water may exist, additional solution processes involving large heats of solutions become possible. Possible reactions of this nature are the exothermic reactions of carbon dioxide dissolution in water and solvation of silicate particles at any temperature at which water is liquid, and serpentinisation of olivine-type minerals at temperatures about 350 K (Malvoisin *et al.* 2012; Carroll, Slipsky & Mather 1991; Tarasevich 2006). Solvation of carbon dioxide and wetting of silica would give temperature rises of order 1 K at the melting point of water for reasonable estimates of cometary composition, but serpentinisation at plausible olivine:water ratios could give localised heating of order 50 K.

## 7. Conclusion

An interior atmosphere at a significant pressure is a prerequisite for high-volume eruptions from comets, persistence of cometary activity at a significant distance from perihelion, and for existence of liquid phases at any point in a cometary lifetime. We have estimated the likely composition of an atmosphere derived from initial sublimation of outer surfaces of a cometary nucleus and discussed the likely consequences of the existence of such an atmosphere. The principal difference between our estimates and previous work is that we find that pristine comets should fill with gas in the years or centuries after first perihelion due to the low sublimation temperatures of volatile components such as CO, leaving no truly pristine material in the interior. We note that the complexity and processed nature of the observed surface of comet 67P/Churyumov-Gerasimenko, and the high-volume eruptions at far from perihelion distances observed, *inter alia*, from Halley’s Comet at a distance of 14 AU (West *et al.* 1991), are explicable in terms of these consequences, while they are not compatible with a process of ablation of a pristine frozen core. It is time to retire the conception of comets as pristine remnants of the infant solar system and consider them as bodies which have experienced a complex history before coming into our view.

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