

CLATHRATE HYDRATES FORMATION IN COMETARY NUCLEI

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Abstract. The initial composition of current models of cometary nuclei is only based on two forms of ice: crystalline ice for long period comets and amorphous ice for short period comets. A third form of ice, i.e. clathrate hydrate, could exist within the short period cometary nuclei, but the area of formation of this crystalline structure in these objects has never been studied. Here, we show that the thermodynamic conditions in the interior of short period comets allow the existence of clathrate hydrates in Halley Type Comets. We show that their existence is viable in the Jupiter Family Comets only when the equilibrium pressure of CO clathrate hydrate is at least one order of magnitude lower than the usually assumed theoretical value. The amount of volatiles that could be trapped in the clathrate hydrate layer may be orders of magnitude greater than the daily amount of gas released at the surface of the nucleus at perihelion. The formation and the destruction of the clathrate hydrate cages could then explain the diversity of composition of volatiles observed in comets.

1 Introduction

Cometary nuclei are now regarded as the most primitive objects in the solar system. However, their physical characteristics remain unknown. Models of cometary nuclei (e.g. Espinasse et al. 1991; Enzian et al. 1997; Orosei et al. 1999; Capria et al. 2003; Prialnik et al. 2004; Mousis et al. 2005; Huebner et al. 2006) consider only two types of ice structure in these objects: crystalline when the nucleus was formed in the protoplanetary disk (long-period comet), amorphous when it comes from the transneptunian region (short period comet). A third structure of ice, called clathrate hydrates (hereafter “clathrate”), could exist within the cometary nuclei (Delsemme and Swings 1952; Schmitt and Klinger 1987; Smoluchowski 1988; Prialnik et al. 2004; Huebner et al. 2008). The formation of such structures within the cometary nuclei may change their physical behavior and contribute to the physical diversity observed in the comets in the same way as their orbital and collisional history and their formation location.

A model of comet nucleus with such a structure of ice has already been developed (Flammer et al., 1998), but the physics on which it is based is incorrect: this model considers that the icy matrix of cometary nucleus was entirely composed of clathrates and that their dissociation occurred only during the sublimation of H₂O ice. The possible formation of clathrates and their location inside the short period comets has been discussed by Schmitt and Klinger (1987) but has never been studied, certainly because they are initially completely composed of amorphous ice. However, experiments by Bar-Nun et al. (1988), Blake et al. (1991) and Schmitt et al. (1992) showed that the crystallization of amorphous ice with volatile molecules trapped inside creates clathrates.

In the present work, we demonstrate that thermodynamic conditions for the formation of clathrates are met within the short period comets. The short-period comets are divided into two categories which we studied separately: the Halley Type Comets (periods between 20 and 200 years; hereafter HTC’s) and the Jupiter Family Comets (period less than 20 years; hereafter JFC’s) represented in this work by the orbits of comets 1P/Halley and 67P/Churyumov-Gerasimenko respectively. We discuss the implication of the presence of clathrates in the physics of cometary nuclei. Their formation could explain the diversity of composition of volatiles observed in comets and outbursts that take place before the perihelion passage of some nuclei. Note that the model presented here does not form clathrates within the porous network. The following study is based on a comparison between the equilibrium pressure of clathrate and that of the gaseous phase in the porous network.

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2 Nucleus model

The nucleus model employed in this work is based on the one-dimensional model developed by Marboeuf et al. (2009a,b). The model considers an initially homogeneous sphere composed of a predefined porous mixture of ices (essentially water ice) and dust in specified proportions. It describes heat transmission, gas diffusion, sublimation/recondensation of volatiles within the nucleus, dust release and mantle formation. Water ice is initially amorphous. A fraction of the volatiles can be trapped in the water ice matrix, while the remaining form pure condensates in the pores. When heated, the fraction of volatiles condensed in the pores sublimates first, and then the other fraction trapped within the matrix is released during the transition from amorphous to crystalline water ice.

3 Thermodynamic parameters and initial composition

We assume that all the objects share a similar composition and have identical thermodynamic parameters at the beginning of the computation, regardless their formation location. The initial ice phase of our models is assumed to be composed of a mixture of amorphous water ice (Taylor 1992; Kouchi et al. 1994) with CO and CO₂, which are the most abundant volatile species observed in cometary nuclei (Bockelée-Morvan et al. 2004). The amorphous to crystalline ice phase transition is exothermic and irreversible¹.

The parameters adopted for our study are the mole fractions CO/H₂O and CO₂/H₂O respectively equal at 15% and 5%. The nucleus porosity is assumed to be equal at 50% and we adopt 770 J.kg⁻¹.K⁻¹ and 4 W.m⁻¹.K⁻¹ for the Heat Capacity and heat conductivity of dust's grains.

The presence of several volatile compounds in the gas phase of the porous network could generate the formation of a multiple guest clathrate (hereafter MG clathrate) whose equilibrium pressure varies as a fonction of the gas phase composition and the temperature. The equilibrium pressure of the MG clathrate P_c is given by (Hand et al. 2006):

$$P_c = \left(\sum \frac{y_i}{P_i^c} \right)^{-1} \quad (3.1)$$

where y_i is the mole fraction of the volatile i in the gas phase and P_i^c the equilibrium pressure of the corresponding clathrate. The equilibrium pressure curves of CO and CO₂ are derived from Lunine & Stevenson (1985) (Hersant et al. 2004). When the gas pressure is higher than the equilibrium pressure of the MG clathrate, the clathration of the volatiles in the pores becomes possible.

4 Results

4.1 Halley Type Comets

Figure 1 represents the evolution of the stratigraphy of a HTC over a 300 yr period. It shows that the stability zone of the MG clathrate can extend from the amorphous-to-crystalline water ice zone to the surface of the nucleus, the size of this zone depending on the location of the comet on its orbit. When the comet approaches perihelion, the amorphous layers crystallize and the CO and CO₂ released in the pores can be enclathrated by crystalline water ice available on their surface. However, at perihelion, due to the increase of temperature, the MG clathrate equilibrium pressure increases faster than the gas pressure and exceeds it, then leading eventually to the dissociation of the clathrates. Because the dissociation kinetics of clathrates is poorly known, it is indeed impossible to determine whether the dissociation is effective or not in comets. On the other hand, when the comet moves away from perihelion, approaches aphelion and then comes back toward the Sun during a timespan of ~ 70 yr, the equilibrium pressure of the MG clathrate becomes lower than the gas pressure in the pores, favoring again its formation in the porous network, provided that there is free crystalline water ice.

When the comet approaches perihelion, the clathration of volatiles is kinetically favorable because H₂O molecules are highly mobile, due to the crystallization of amorphous water ice (Blake et al. 1991; Schmitt et al. 1992). Hence, if a clathrate layer succeeded to form in the pores during the nuclei crystallization, the formation

¹Note that Kouchi & Sirono (2001) have shown that crystallization of amorphous mixtures of water ice and some other molecules can become endothermic.

of additional layers of clathrates should be favored at later times on the orbit because the nucleation process eases the formation of new cages. If the formation of clathrates is effective in HTC along their orbits, then the amount of volatiles trapped and released during their formation/dissociation in the porous network may represent up to 2,400 times the masses of CO and CO₂ and 60 times that of H₂O produced daily at perihelion, assuming a full conversion of H₂O ice into clathrate in the stability zone and complete cage filling.

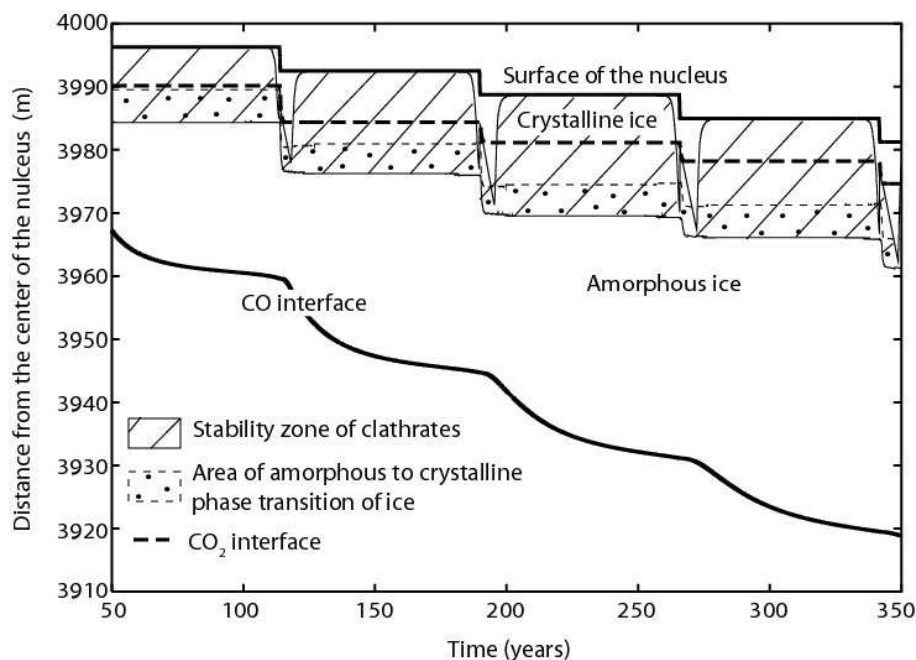


Fig. 1. Stratigraphy of a HTC nucleus as a function of time. The lines represent the surface and the minimum depths at which solid CO₂ (dashed line) and CO (bold solid line) exist. The dotted area corresponds to the zone where the amorphous-to-crystalline water ice phase transition occurs and the dashed area to the zone of the MG clathrate stability.

4.2 Jupiter family comets

We have first found that the clathration of volatiles in the porous network occurs only sporadically in a small area of the nucleus. Lunine & Stevenson (1985) acknowledge that their formula for the equilibrium pressure of CO clathrate is not very well constrained, and Fig. 6 of that paper shows that adding the dipole-dipole interaction in the model lowers the equilibrium pressure by as much as a factor of five. So we have conducted a second test for a JFC over a 60 yr timespan with an equilibrium pressure of CO clathrate which has been divided by 10 with respect to the value given in Hersant et al. (2004). The results have shown that the clathration and crystallization zones are almost superimposed and are located within the stability area of solid CO₂ condensed in the pores. For this family of comets, this implies that the formed clathrate only incorporates CO because CO₂ remains condensed in solid phase in the porous network. The thickness of the clathration zone slightly oscillates with time as a function of the Sun distance and never vanishes. When approaching the Sun, the clathration zone decreases, and inversely, it increases as the nucleus cools. The maximum amount of volatiles trapped or released during the formation or dissociation of CO clathrate in the porous network may represent up to 8,600 times the mass of CO and 2,900 times that of H₂O produced daily at perihelion.

5 Discussion and Conclusions

We have shown that, provided the kinetics of clathrate formation is fast enough, HTC's incorporate a clathrate layer in their interiors most of the time during their orbital evolution around the Sun. The formation of clathrates in JFCs is also possible but we had to assume an equilibrium pressure of CO clathrate that is one magnitude order lower than usually estimated to get a persistent stability zone in the nuclei. On the other hand, molecules such as methane or ethane that exist in lower abundances in coma can also form clathrates in cometary nuclei and their respective equilibrium curves are closer to that of the modified equilibrium curve of CO clathrate. This implies that, in any case, a clathrate layer is likely to exist in JFCs. If a deep clathrate layer does exist, our results suggest that the composition of the coma could be different from that of the gas released in the pores during the crystallization of the amorphous matrix. The formation of a CO-rich clathrate layer in the nucleus could imply the decrease of the outgassing rate of this species and lead to a higher CO₂/CO ratio in the coma than in the gas released in the nucleus itself.

The kinetic of clathrates formation or dissociation is still poorly constrained. The physical parameters that may affect kinetic are multiple (activity of the ice, temperature, difference between the gas pressure and the equilibrium pressure of the clathrate, ...). At low temperature, the formation rate of clathrates must be relatively slow but could anyway take place because the pressure and temperature conditions are favorable and stable over long time periods for both families of comets. Moreover, the formation of clathrates during crystallization of amorphous ice could ease the formation of new cages thereafter, due to the high mobility of water molecules. However, in the absence of more detailed knowledge of the kinetics, it is difficult to assess the relative amount of volatile molecules outgassing and trapped on the long term even during perihelion approach.

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