

LABORATORY STUDIES OF COMETARY ICE ANALOGUES

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ABSTRACT

Laboratory studies have been performed in order to simulate the physico-chemical processes that are likely to occur in the near surface layers of short and intermediate period comets. Pure H₂O ice as well as CO:H₂O, CO₂:H₂O, CH₄:H₂O, CO:CO₂:H₂O and NH₃:H₂O ice mixtures have been studied in the temperature range between 10 and 180 K. The evolution of the composition of ice mixtures, the crystallization of H₂O ice as well as the formation and decomposition of clathrate hydrate by different processes have been studied as a function of temperature and time.

Using our results together with numerical modeling (Espinasse et al., this volume) predictions are made about the survival of amorphous ice, CO, CO₂, CH₄ and NH₃ in the near surface layers of short period comets. The likelihood of finding clathrate and molecular hydrates is also discussed. It is proposed that the analytical methods developed here could be fruitfully adapted to the analysis of returned comet samples.

Keywords: Laboratory Studies, Ices, Clathrate hydrate, Comet Nucleus, Chemical differentiation, ROSETTA mission.

1. INTRODUCTION

The assessment of the scientific potentialities of the ROSETTA-Comet Nucleus Sample Return mission needs a physically based model of the possible structure and composition of the nucleus material in the near surface layers. The choice of the target-comet and of the precise drilling site should strongly depend upon the probability of finding ices in the three first meters. Among the most important questions concerning the near surface layers are the survival of volatile molecules and the structure of the icy component (amorphous, crystalline, clathrate hydrate, molecular hydrate?). Such informations are also extremely important for the design of the driller and the definition of the drilling, retrieval, storage and transport conditions of the samples.

In order to give a physical basis to the phenomena taken into account in advanced numerical models we performed laboratory experiments simulating some of the physico-chemical processes that are likely to occur in comet nuclei. Especially, we studied the evolution of the composition of CO:H₂O, CO₂:H₂O, CH₄:H₂O, CO:CO₂:H₂O and NH₃:H₂O ice mixtures, the crystallization of H₂O-rich ices as well as the formation and decomposition of clathrate hydrate by different processes (co-condensation, crystallization of amorphous ice mixtures and gas-ice interaction). All these processes have been studied as a function of temperature (mainly between 10 and 180 K) and time (up to 20 days). The experimental procedures have been described elsewhere together with preliminary results (Refs. 1-3). Both the composition and the structure of the icy component of the near surface layers are tentatively predicted for short period comets using our results together with the numerical model of Espinasse et al. (Refs. 4-6).

2. EXPERIMENTAL RESULTS

2.1 Thermal evolution of water-rich ice mixtures

Experiments which directly follow the evolution of CO:H₂O, CO₂:H₂O, CH₄:H₂O and NH₃:H₂O ice mixtures as a function of time and temperature have been performed in the laboratory. Samples 0.1 to 5 micron thick are condensed at low temperature (usually 10 K) and the initial composition (gas/H₂O ratio) ranges between 1 and 50 %. The composition of the solid phase is measured by means of infrared transmission spectroscopy (integration over the fundamental vibrational bands). The evolution of the ice mixtures is monitored by performing successive annealing steps at a fixed temperature T_a. A spectrum is then recorded after each annealing step.

The heating sequences of our first experiments were designed to determine the temperature ranges of the evolution processes (Figure 1) while all the following samples were subjected to very long heating steps (up to 20 days) at constant temperature in order to independently understand the time and temperature dependences of the various evolution processes (Figure 2).

For CO:H₂O, CO₂:H₂O and CH₄:H₂O ice mixtures we found that the concentration of volatile molecules in the sample decreases mainly in two temperature ranges with a possible additional, but extremely slow, evolution in the intermediate range (Figure 3). Under vacuum conditions (P < 10⁻⁶ mbar) the first evaporation starts at 25 K for CO, 32 K for CH₄ and about 70 K for CO₂. The evaporation rate strongly depends on both the gas fraction and the temperature but the final gas/H₂O ratio in the ice always ranges between 7 and 10% independently of the initial ice composition (for initial gas/H₂O > 10 %, Figure 4). This "stable" composition is reached above about 50 K for CO. Further increases in temperature lead only to very small gas loss but limitations in long term stability (over days) of our system allow us only to give a maximum CO evaporation rate of 0.2 % per day at 100K for CO:H₂O ices.

When the temperature of the sample is raised above about 120 K a second temperature dependent evaporation starts leading to the complete disappearance of CO, CO₂ or CH₄ in the ice; the final gas/H₂O ratio is below our detection limit : < 0.01 % for CO and CH₄, < 0.001 % for CO₂. This evaporation is triggered by the ice crystallization occurring at the same time as deduced from the fact that the time necessary for the complete depletion of the volatile molecules from the ice is independent on the molecule and is clearly correlated with the crystallization rate of ice (see 2.2 and Figure 5). With ternary CO:CO₂:H₂O ice mixtures an intermediate formation of metastable clathrate hydrate has been observed (see part 2.3) but after decomposition only pure crystalline H₂O ice remains.

The evolution of NH₃:H₂O ice mixtures have also been studied. The main result is that NH₃ molecules are not able to diffuse through water ice at temperature as high as 170 K. They begin to evaporate only a few degrees before H₂O. The formation of ammonia hydrate with strong hydrogen bonds explains this behaviour.

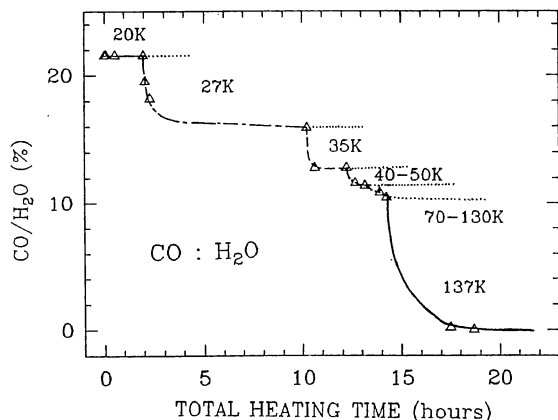


Fig. 1: Evolution of the CO content (%) versus total heating time of a CO:H₂O ice mixture (initial CO/H₂O ratio = 22 %). Successive heating steps at constant temperature.

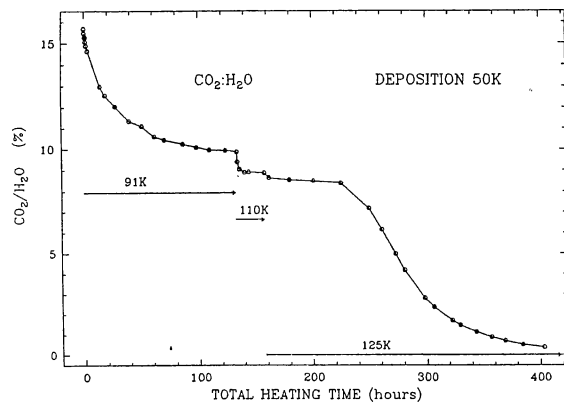


Fig. 2: Evolution of the CO₂ content (%) versus total heating time of a CO₂:H₂O ice mixture (initial CO₂/H₂O ratio = 16 %). Three successive heating steps at constant temperature (91 K, 110 K and 125 K).

2.2 Crystallization rate of H₂O-rich ices

The crystallization rate of pure water ice and ice mixtures (CO:H₂O, CO₂:H₂O, and CO:CO₂:H₂O) has been measured as a function of temperature. The experiments have been performed at constant temperature in the 125 - 150 K range. The CO or CO₂ molecule concentration just before crystallization ranged between 0.5 and 7%. The time necessary to crystallize an amorphous ice sample at temperature T is determined by analyzing the time evolution of the shape and position of both the 3.1 and the 6.0 μm infrared absorption bands of H₂O (Ref. 7).

The time $t_c(T)$ defined in this way corresponds to an almost complete crystallization (no more changes in the absorption bands) although it is not possible to quantify precisely (in percent) the effective extent of the amorphous-crystalline conversion by infrared spectroscopy. For the water-rich ice mixtures the time $t_c(T)$ necessary to deplete the ice in CO or CO₂ molecules (to less than 0.01 %) during the crystallization stage has also been measured. The results for $t_c(T)$ and $t_d(T)$ are plotted on Figure 5. The crystallization times for pure and mixed ices are well correlated in an Arrhenius plot ($\log(t) = f(1/T)$), except for the two ternary CO:CO₂:H₂O ice mixtures. These ternary mixtures showed to behave quite differently from the simple binary mixtures of H₂O with either CO or CO₂; they first formed a clathrate structure before losing their trapped CO and CO₂ molecules. This case will be analysed in the next paragraph and is not taken into account in the following discussion.

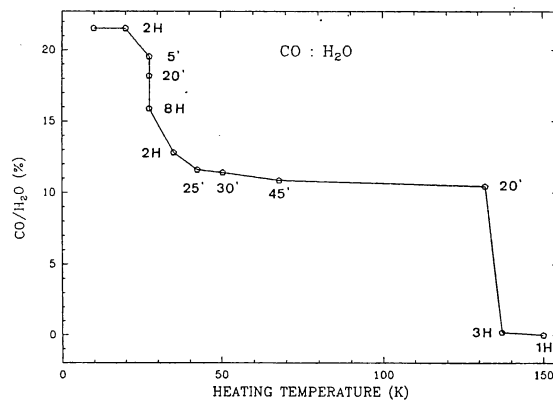


Fig. 3: Evolution of the CO content (%) versus temperature of a CO:H₂O ice mixture (initial CO/H₂O ratio = 22 %). The time noted at each point is the maximum annealing time at the corresponding temperature.

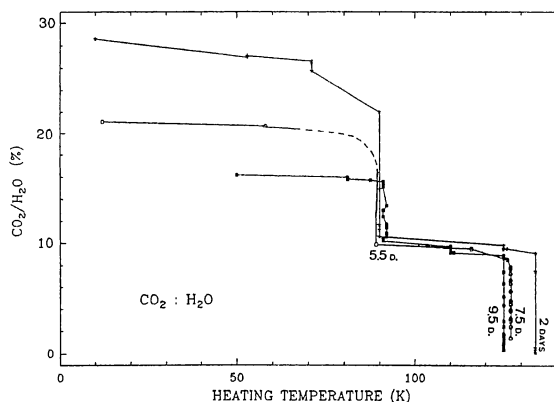


Fig. 4: Evolution of the CO₂ content (%) versus temperature of CO₂:H₂O ice mixtures with three different initial CO₂/H₂O ratios (16 %, 21 % and 29 %). The successive points at a same temperature correspond to measurements as a function of time at constant temperature. The maximum annealing times are shown for some typical temperatures.

The crystallization time ranges from about 8 days at 125 K to less than 5 minutes at 150 K. The activation law linking the time t_c for almost complete crystallization and the temperature T is:

$$t_c = A \cdot e^{-E_a/kT}$$

where A is a constant:

$$A = 2.65 \cdot 10^{-17} \text{ hour}$$

$$-E_a/k = 5370 \text{ K}$$

The CO and CO₂ depletion times $t_d(T)$ under vacuum ($P < 10^{-6}$ mbar) are virtually the same at a given temperature and are very well correlated with the crystallization times. They are about 2 to 3 times larger which suggest that the evaporation is triggered and controlled by the ice crystallization. The extrapolation of the activation law at lower temperatures gives crystallization times of about 5 years at 110K, 500 years at 100 K, 10^5 years at 90 K and $5 \cdot 10^9$ years at 80 K.

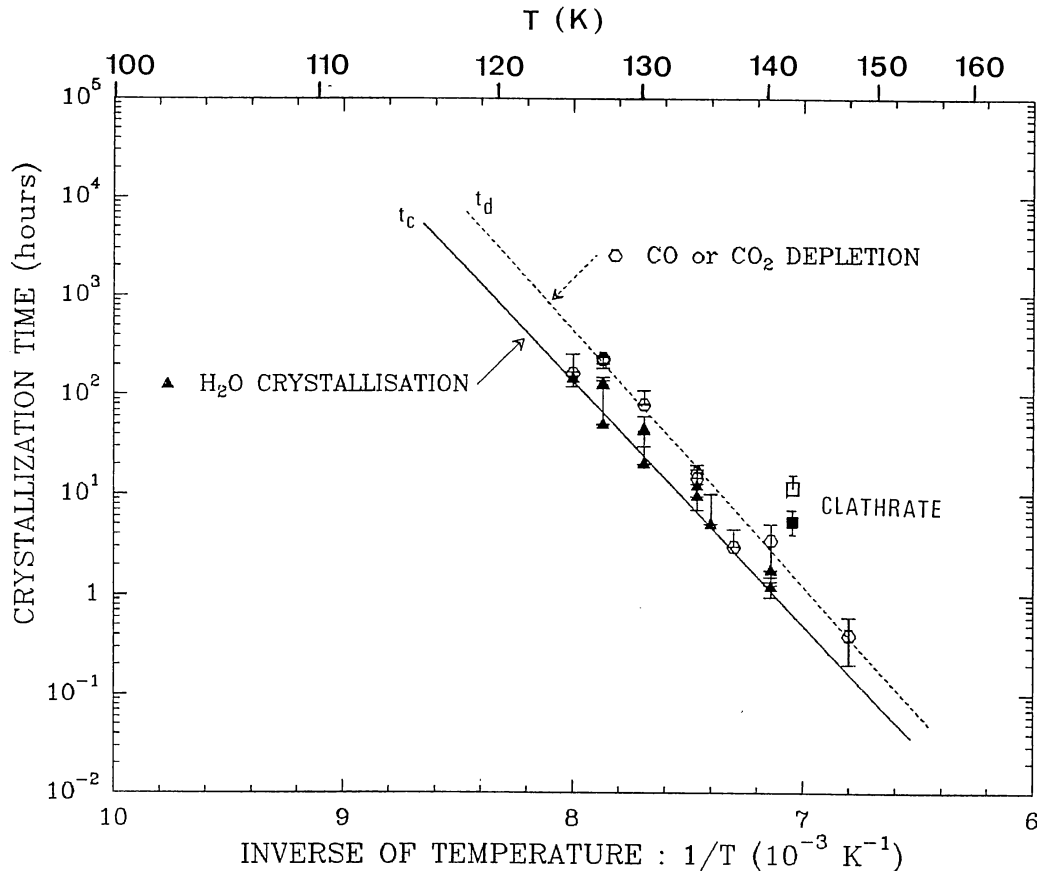


Fig. 5: Crystallization time of amorphous H_2O ice (Black triangle - Solid line) and CO or CO_2 depletion time (White hexagon - Dotted line) versus temperature for $\text{CO}:\text{H}_2\text{O}$ and $\text{CO}_2:\text{H}_2\text{O}$ ice mixtures. The black and the white squares correspond to formation and decomposition times of clathrate hydrate as measured for a $\text{CO}:\text{CO}_2:\text{H}_2\text{O}$ ice mixture.

2.3 Clathrate hydrate formation and decomposition

Different processes which can lead to the formation or the decomposition of clathrate hydrate have been studied in the laboratory.

First the simultaneous condensation of CO and CO_2 with H_2O at low pressure ($P < 10^{-4}$ mbar) and low temperature (10 - 100 K) showed that no clathrate structure is formed under these conditions. The ice mixtures obtained by this way have an amorphous structure, as demonstrated by the broad $3.1 \mu\text{m}$ absorption band of H_2O , and a composition mainly depending on the gas mixture composition and on the deposition temperature. Indeed, the deposition of a $\text{CO}:\text{H}_2\text{O}$ gas mixture with 20 % of CO leads to an ice composition with almost 20 % CO for a deposition temperature of 10 K, 18 % for deposition at 30 K and less than 2 % when condensed at 50 K. It is then quite clear that clathrate hydrate, which has a crystalline structure with a defined composition cannot be formed by simultaneous condensation below 100 K. However, it has been shown by Bertie and Devlin (Ref. 8) that around a condensation temperature of 120 K a clathrate structure can be formed by simultaneous condensation of H_2O and oxirane (moderately volatile) in a ratio close to the clathrate formula. Although we did not extend the experiments above 100 K, it seems impossible to trap a sufficiently large amount of CO or CO_2 in crystalline H_2O ice when condensing under low gas pressure as a result of their large volatility above 120 K. A partial gas pressure probably higher than 0.1 mbar for CO_2 and 200 mbar for CO would be necessary to form a clathrate structure by condensation at 120 K. Experiments have to be done in order to assess this possibility.

The second process expected to be able to form clathrate is the crystallization above 100 K of an amorphous ice mixture condensed at low temperature. It has been shown that the crystallization under vacuum ($P < 10^{-6}$ mbar) of simple binary $\text{CO}:\text{H}_2\text{O}$ or $\text{CO}_2:\text{H}_2\text{O}$ ice mixtures leads to the complete evaporation of the molecules still trapped in the ice. The formation of a stable clathrate structure is then impossible under these conditions.

However, for the experiments performed with ternary $\text{CO}:\text{CO}_2:\text{H}_2\text{O}$ ice mixtures a quite different behaviour has been observed during crystallization. Instead of a monotonic decrease of the CO and CO_2 band strengths with time during crystallization, a new CO_2 absorption band (at $4.25 \mu\text{m}$) progressively appeared close to the normal CO_2 absorption (at $4.28 \mu\text{m}$) while this last band decreased in intensity. The new band is characteristic of CO_2 molecules trapped in the small cages of a clathrate structure as recently shown by Fleyfel and Devlin (Ref. 9). We estimated the fraction of H_2O ice converted into clathrate to be about 10 %. Under vacuum conditions the time of clathrate formation is about 5 hours at 142 K. However, at 142 K the formation step is immediately followed by a progressive loss of the CO and CO_2 molecules leading to the decomposition of the clathrate structure in about the same time (Figure 5). At 125 K the formation and decomposition processes are much slower but the clathrate structure is still unstable under vacuum conditions. It is likely that the addition of a CO_2 gas pressure close to the dissociation pressure of the clathrate would tend to stabilize the clathrate structure formed. However, as soon as the gas pressure drops below the dissociation pressure a decomposition should occur as we will show below.

A third possibility for clathrate formation we studied in the laboratory is by interaction between molecules in the gas phase and pure crystalline H₂O ice. A large number of experiments have been performed for the formation of CO₂ clathrate between 195 and 215 K (Ref. 1). The main results are that clathrate hydrate forms only when the gas pressure is higher than the dissociation (or equilibrium) pressure $P_c(T)$ of the corresponding clathrate, and that the clathrate structure decomposes as soon as the pressure drops below $P_c(T)$. The phase diagram showing the temperature dependence of the dissociation pressure $P_c(T)$ of the CO₂ clathrate is known between 150 and 273 K. In Figure 6 we have reviewed all the data available in the literature for clathrates with a single host molecule.

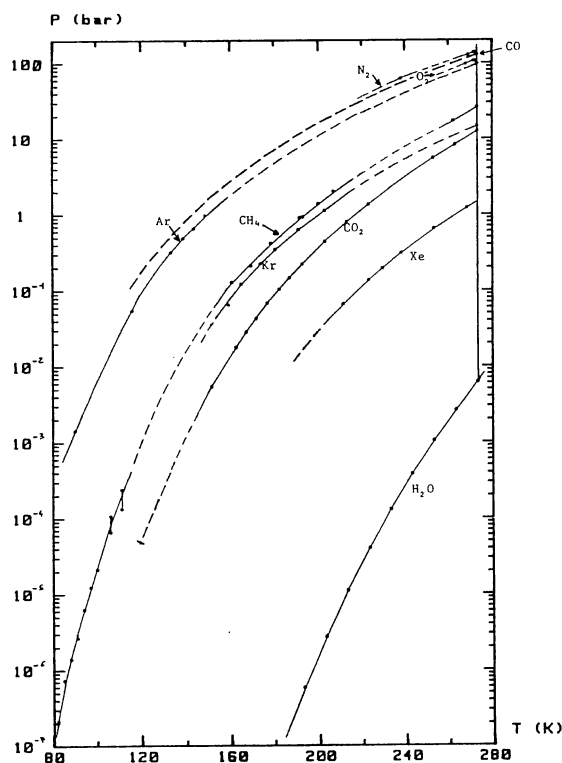


Fig. 6: Phase diagram $P_c(T)$ of some single host clathrate hydrates. Dots are experimental values, solid lines are interpolations and dashed lines are extrapolations.

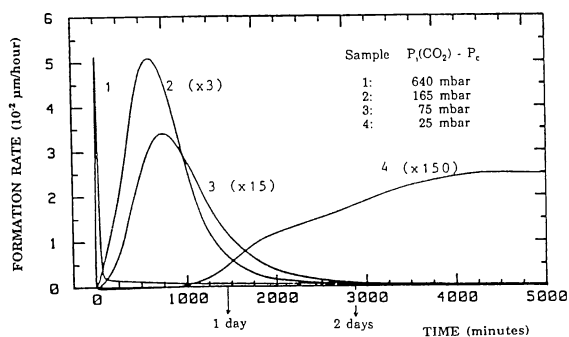


Fig. 7: Formation of CO₂ clathrate hydrate by gas-ice interaction at 195 K ($P_c = 260$ mbar). Influence of the gas pressure. The formation rates have been multiplied by the factors between brackets.

The formation rate of clathrate hydrate has been found to mainly depend on: i) the difference between the gas pressure P and the dissociation pressure P_c at a given temperature T (Figure 7), ii) the surface area of the grains and, iii) the stability of the ice surface (which depends in part on temperature). In the temperature range investigated (195 K - 215 K) the mean growth rate measured for the CO₂ clathrate is about 10^{-4} $\mu\text{m}/\text{hour}$ per millibar over the dissociation pressure $P_c(T)$. A clathrate layer one micron thick will need more than one month to build up with one millibar overpressure. At lower temperature the formation rate is probably one to several orders of magnitude smaller, but up to now no experimental data exists below 195 K. Furthermore, the decomposition rates also depend on the difference between the pressure P and $P_c(T)$ and are 10 to 30 times larger than the formation rates. It can be deduced from these results that the formation and the stabilization of a clathrate structure over large time scales is only possible under restricted physical conditions.

3. THE NEAR SURFACE LAYERS OF COMETS

In the following we will use the results of the numerical modeling of comet nuclei of Espinasse et al. (Ref. 4-6). This advanced model already takes into account our results on the temperature evolution of binary ice mixtures and on the crystallization of amorphous ice in the calculation of both the thermal profile and the chemical differentiation of the nucleus. For the processes which are not yet included in the model we will estimate their occurrence from both thermal and internal pressure profiles. Indeed, if we consider the time dependence of the temperature profile in a nucleus on a given orbit it is possible to derive the temperature variation of a given layer as a function of time. Especially, the thickness of near surface material which has already been subjected to a temperature higher than a given value T for more than a given time t can be estimated.

For a nucleus on an orbit identical to that of P/Churyumov-Gerasimenko (period: 6.5 years, perihelion: 1.29 A.U., aphelion: 5.72 A.U.) the model shows that the temperature of the 10 first meters below the surface never drops below 130 K and that the top 3 meters of icy material are subjected to temperatures higher than 150 K for more than one year during each revolution of the comet. The above temperatures are lower limits found for the combination of various initial nucleus compositions (CO/H₂O = 5 % and 30 %, or CO₂/H₂O = 5 % and 15 %) and porosities (30 % and 80 %). Furthermore, in all these cases the model gives a CO free crystalline ice layer thicker than 10 meters and a CO₂ free layer between 3 and 10 meters for the second revolution after the capture of the comet in its short period orbit. However, the model also shows that for a comet on an orbit like P/Halley CO₂ can be found in some cases at less than half a meter below the surface (Refs. 4, 5).

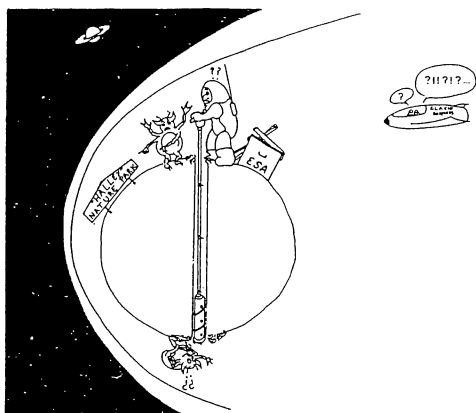
Let now consider the "clathrate hydrate problem" on the basis of our experimental results. First it should be emphasized that the presence of clathrate hydrate in comet nuclei depends on the possibility to form and to stabilize such a compound either during or after the formation of comets. In this last case the physical conditions prevailing inside the nucleus have to be taken into account. If comets are formed below 100 K we can safely exclude the initial formation of clathrate hydrate because the icy component of the nucleus will have an amorphous structure. For higher formation temperatures the partial pressures need to be higher than the dissociation pressures of the clathrates. We calculated that the number density of CO₂ and CO have to be larger than 10^{15} and 10^{18} molecule/cm³ respectively in order to fulfil the first condition for clathrate formation. This is several orders of magnitude larger than the values currently used for the presolar nebula density at the places of possible comet formation.

After the formation of a comet, clathrate hydrate can only form in the crystalline layers or in the layers in the course of crystallization. Although pure CO clathrate is excluded as a result of its high dissociation pressure above 120 K ($P_c > 200$ mbar) a mixed CO₂ clathrate with some CO, CH₄, Ar and N₂ molecules could form by crystallization above 100 K. The problem of its stability is difficult to assess due to the lack of experimental data. Especially, we do not know the partial pressures necessary to stabilize the very volatile components, such as CO, CH₄, Ar and N₂, in mixed clathrates.

However, if we take into account the fact that the dissociation pressure of a single host clathrate is almost always smaller than the saturation pressure of the host molecule as a pure solid we can conclude that a given clathrate, if formed, will survive at temperature slightly higher than the pure solid. For pure CO₂ clathrate this temperature shift is 6 K around 140 K. We have seen that the numerical model (Refs. 4-6) gives a recondensation of CO₂ on the crystalline ice grains up to depths as low as 0.5 meter from the surface. We should then expect CO₂ clathrate to be stable in at least the same layers. The amount of clathrate hydrate compared to hexagonal or cubic water ice is probably lower than 20 % because of, i) the limited amount of CO₂ trapped in the ice before crystallization (7 to 10 %), ii) a partial loss of CO₂ during the crystallization of the clathrate, iii) a probable partial decomposition of the clathrate at higher temperature. More laboratory data together with a numerical modeling of these processes are necessary to give both the location and concentration of clathrate hydrate in comet nuclei as well as its effect on the gas production rates.

4. CONCLUSION

In summary, it can be concluded that the 3 first meters of short and intermediate period comet will be composed of crystalline H₂O ice almost certainly without very volatile molecules such as CO, CH₄, N₂ and Ar. The volatile molecules could be found only in the gas phase (in the nucleus porosity) except for CO₂ (with perhaps H₂S) which could have locally formed a clathrate hydrate structure or could have recondensed in the upper layers up to very close to the surface of the icy material. NH₃ and perhaps HCN molecules will be found as hydrates at the top of the ice layer of the nucleus together with all other less volatile molecules.



TOO DEEP OR NOT TOO DEEP ?

THAT IS THE QUESTION !

Many uncertainties remain because experimental data are still lacking for some processes and/or in critical temperature and pressure ranges. Especially, all the experiments described in part 2 have to be performed under moderate gas pressures (10⁻³ to 10 mbar) in order to more closely simulate the physical conditions prevailing inside the nucleus. The results could be quite different for the trapping of gases in ice or clathrate. The formation conditions and the stability of mixed CO and CO₂ clathrate need also to be more thoroughly studied.

On the other side, the numerical model needs to be completed by adding dust in the nucleus, a crust formation at the surface and the rotation of the nucleus as well as the future experimental data about the evolution processes of cometary materials.

5. ACKNOWLEDGEMENTS

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