Trapping of gas mixtures by amorphous water ice

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Our studies on gas trapping in amorphous water ice at 24–100 K were extended, by using mixtures of CH_4, CO, N_2, and Ar, rather than single gases. In 1:1 gas:(water vapor) mixtures, the competition among these gases on the available sites in the ice showed that the trapping capacity for the various gases is determined not only by the structure and dynamics of the ice, but is also influenced by the gas itself. Whereas at 24–35 K all four gases are trapped in the ice indiscriminantly, at 50–75 K there is a clear enhancement, in the order of $CH_4 > CO > N_2 \gtrsim Ar$. This order is influenced by the gas-water interaction energy, the size of the trapped gas atom or molecule, the type of clathrate-hydrate formed (I or II) and, possibly, other factors. It seems that the gas can be trapped in the amorphous ice in several different locations, each being affected in a different way by the deposition temperature and gas composition. Once a gas atom or molecule is trapped in a specific location, it is predestined to emerge in one of eight different temperature ranges, which are associated with changes in the ice. The experimentally observed enhancements, together with the findings on the gas composition of comet Halley, might enable an estimation of the gas composition in the region of comet formation.

I. INTRODUCTION

In our previous studies on the trapping of various gases in thin layers of cold (18–100 K) amorphous water ice and their stepwise release from it upon warming, we learned much about the structure and dynamics of the ice:[1-3] The release of the gas from the ice in 8 separate temperature ranges [(a)–(g)] was attributed to various processes which take place in the slowly warming (~ 1 K min^{-1}) ice. Thus it was found that the amorphous ice anneals irreversibly in three separate steps: 35–80 K (b), 80–100 K (d), and 120–130 K (d'). At 137 K (e) it transforms into cubic ice and at 160 K (f) into hexagonal ice. The last range of gas release, at about 180 K (g), along with the evaporation of the ice, is attributed to the evaporation of a clathrate-hydrate of the gas. The first two ranges, starting at ~ 26 K (a) and 44 K (c), are attributed to the evaporation of frozen gas and the desorption of a monolayer of the gas from the surface. The amorphous ice is needlelike, like a shaggy woolen carpet and extremely porous. Hence its large surface area—90 m^2 g^{-1} (Ref. 2) or even 258 m^2 g^{-1}.[4] It was also found that when a large quantity of gas is trapped in the ice (gas-to-ice ratio ≈ 1) below 50 K, its release from the ice is accompanied by the shattering of the ice and the ejection of numerous ice needles, each containing about 10^{10} water molecules, which are propelled by gas jets, each containing about 5×10^{10} gas atoms. A dynamic percolation process was suggested to explain this behavior.[3]

The shattering of the ice during massive gas release upon warming, together with a thermal model of a comet nucleus, describing the penetration of a heat wave into the nucleus, enabled us to propose a mechanism for the formation of the active craters which were observed on the nucleus of comet Halley.[5]

The gases studied previously were Ar, H_2, D_2, and Ne, with a few experiments with CO, CH_4, N_2, and CO_2. Each gas was trapped *separately* in the ice, serving merely as an indicator to the processes which take place in the ice itself. In the present study, we trapped *mixtures* of Ar, CO, CH_4, and N_2 in the ice, in order to gain some insight into the interaction of these gases with the ice, through their competition with each other. Another motivation for using gas mixtures was the possible elucidation of the gas composition of the solar nebula in which, presumably, the coments were formed. It was expected that the experimental findings, together with the newly acquired knowledge on the gas composition of the nucleus of comet Halley[6,7] would enable us to suggest what the composition of the nebula might have been.

II. EXPERIMENTAL

The experimental setup is identical to the one used in our previous studies.[2,3] Onto a cryogenically cooled plate ($5 \times 3.5 \times 0.5$ cm^3), in a cryogenically pumped chamber (at 10^{-8} Torr), were flowed gas-water vapor mixtures through a capillary tubing, with a diffuser on its tip. Each gas-water vapor mixture was prepared by distilling thoroughly degassed water into a 2 l glass bulb, until a liquid was formed. Thus, a constant water vapor pressure of ~ 20 Torr was assured. A single gas or a mixture of two or three gases was then added to the bulb, up to a pressure of 40 Torr. The pressure of each gas in a mixture was thus only $\frac{1}{2}$ or $\frac{1}{3}$ of its pressure when single. The following mixtures were used:

$H_2O:CH_4:CO(\text{or } N_2) = 1:0.33:0.33:0.33$,

$H_2O:H_2O:CH_4:Ar:CO(\text{or } N_2) = 35:1:0.33:0.33:0.33$,

$H_2O:CO:CH_4 = 1:0.5:0.5$; $1:1:0.1$; $1:1:0.01$

$$\text{and } 1:1.7\times10^{-2}:1.7\times10^{-4} .$$

In addition, 1:1 mixtures of water vapor with a single gas (CO, CH_4, N_2, or Ar) were deposited, for comparison. In some experiments, pure water vapor was deposited on the plate, and the gas mixture was flowed into it.

Ice layers containing about 10^{19} water molecules cm^{-2} were deposited during 30–45 min at a pressure of $\sim10^{-7}-10^{-5}$ Torr in the chamber (depending upon the temperature) under constant pumping. The pressure of the gas flowing from the capillary tubing and impinging on the plate was constant at 2×10^{-5} Torr.

The plate's temperature during deposition was varied between 24 and 100 K$\pm$1 K. After the deposition was terminated, the chamber was pumped down to $\sim10^{-8}$ Torr and the plate was warmed up, at a rate of ~1 K min^{-1}, until all the ice evaporated, at about 200 K. The fluxes of gases and water vapor evolving from the ice were monitored by a precalibrated quadrupole mass filter, which was connected to a suitably programmed IBM PC computer. The amounts of the various gases evolved in each temperature range were obtained by integrating their flux over the time of their evolution. At the end of each experiment, the calibration of the mass filter was rechecked, by flowing the gas-water vapor mixture into a warm (260 K) chamber and monitoring the fluxes of the various components. A typical plot of gas flux versus temperature is shown in Fig. 1.

III. EXPERIMENTAL RESULTS

The effects of the competition among the various gases of a mixture were determined by comparing the amounts of gas released at each temperature range with the amounts of the other gases in the mixture, as well as with single gases (Figs. 2 and 3). Each point represents an average of at least two experiments. In this study, ranges (a), (b), and (c) could not be separated from each other and are presented as (a + b + c). Since the lowest deposition temperature for the mixtures was 28 K, very little gas was frozen (a), and (a + b + c) is actually (b + c).
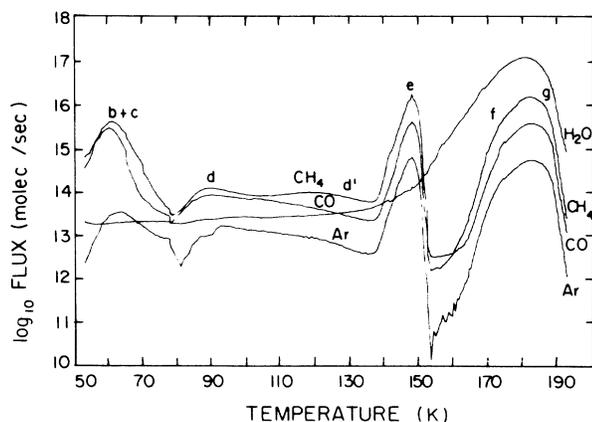
The major results can be summarized as follows.

(1) The total amount of trapped gas decreases by up to 6 orders of magnitude between 24 and 100 K. As 35 K, total gas-to-ice ratios as high as 6 are obtained, with both single gases or gas mixtures (where the three gases are combined together). This gas-to-ice ratio is six times larger than the original 1:1 gas:(water vapor) composition, because during the deposition, a huge number of ice needles is broken from the ice and propelled by gas jets.[3]

(2) At 24–35 K, the major contribution to the total amount of trapped gas is from ranges (b + c) and (e), whereas at 50–100 K the major contribution is shifted to ranges (e), (f), and (g), in the order of (g) > (f) > (e), (d) being small throughout. This shift is obvious, in view of the total absence of gas release in range (c) and the sharp decrease in (b) above 45 K.

(3) At 24–35 K, gas mixtures are trapped in (f) and (g) much less efficiently than when each gas is trapped separately. A similar decrease in (f) and (g) with a single gas (Ar) was observed previously,[2] but at lower temperatures (18–25 K). Thus, the decrease at very low temperatures is enhanced with gas mixtures.

(4) At 24–35 K there seems to be little difference in the trapping efficiencies of the four gases in all the ranges. However, a marked separation appears at 50–75 K: CH_4 dominates in all the gas release ranges, followed by CO.

FIG. 1. A plot of the fluxes of gas and water vapor vs temperature. The gas-rich amorphous ice was condensed at 50 K, from a $H_2O:CH_4:CO:Ar = 1:0.33:0.33:0.33$ mixture. The various ranges of gas evolution (b)–(g) are labeled. Note the changes in gas evolution over 6 orders of magnitude.
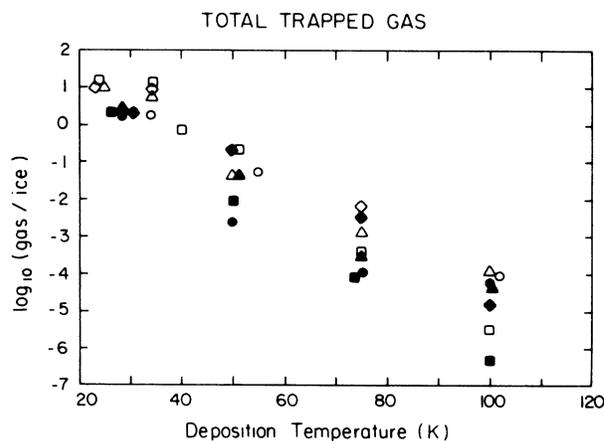
FIG. 2. The total amounts of trapped gases vs deposition temperature of the (water vapor) gas mixtures. $\Diamond$–CH_4, $\triangle$— CO, $\circ$ —N_2, and $\square$—Ar. Open symbols represent the results of the deposition of 1:1 single gas-water vapor. Solid symbols represent the results of the deposition of gas mixtures $H_2O:CH_4:Ar:CO(\text{or } N_2) = 1:0.33:0.33:0.33$. Each point is an average of at least two experiments. (Some points were moved slightly on the temperature scale, to prevent overlapping.)

These two gases are trapped from a mixture to the same extent as when deposited alone. Yet, N_2 and Ar are trapped from a mixture much less efficiently than when deposited alone. Apparently, their places in the ice are taken by the CH_4 and CO. The general order in all ranges is thus $CH_4 > CO > N_2 \gtrsim Ar$. At 100 K, the amounts of trapped gases are small and there seems to be no clear pattern, except that (g) dominates and N_2 is relatively strong.

(5) The competition among the gases in a mixture is much more severe than can be deduced from the results in Fig. 2. At 50 K, the CO/CH_4 ratio is ~ 0.25 for the total trapped gas content from a 1:1 $CO:CH_4$ mixture— an enhancement of CH_4 over CO by a factor of 4. However, only from a gas mixture with a 100:1 $CO:CH_4$ does the CO overtake the CH_4 and the CO/CH_4 ratio of total

trapped gas becomes 2.5. Thus, in this case, the enhancement of CH_4 over CO at 50 K is by a factor of 40. Yet, when the competition between the CO and CH_4 is even more severe, in an experiment where the 100:1 $CO:CH_4$ mixture was flowed for 45 min. at 50 K, into preexisting amorphous ice, rather than being codeposited with it, the CO/CH_4 ratio of total trapped gas was reversed, and became 0.67. In this case the enhancement of CH_4 over CO is by a factor of 150.

In these experiments, the gas-to-water vapor ratio in the codeposited mixture was 1, as was the gas-to-ice ratio in the experiment of gas flow into preexisting ice. However, when a very water-rich mixture $H_2O:CO:CH_4 = 1:1.7 \times 10^{-2}:1.7 \times 10^{-4}$) was codeposited at 50 K, the CO/CH_4 ratio of the total trapped gas was 100, exactly like the ratio in the gas mixture.
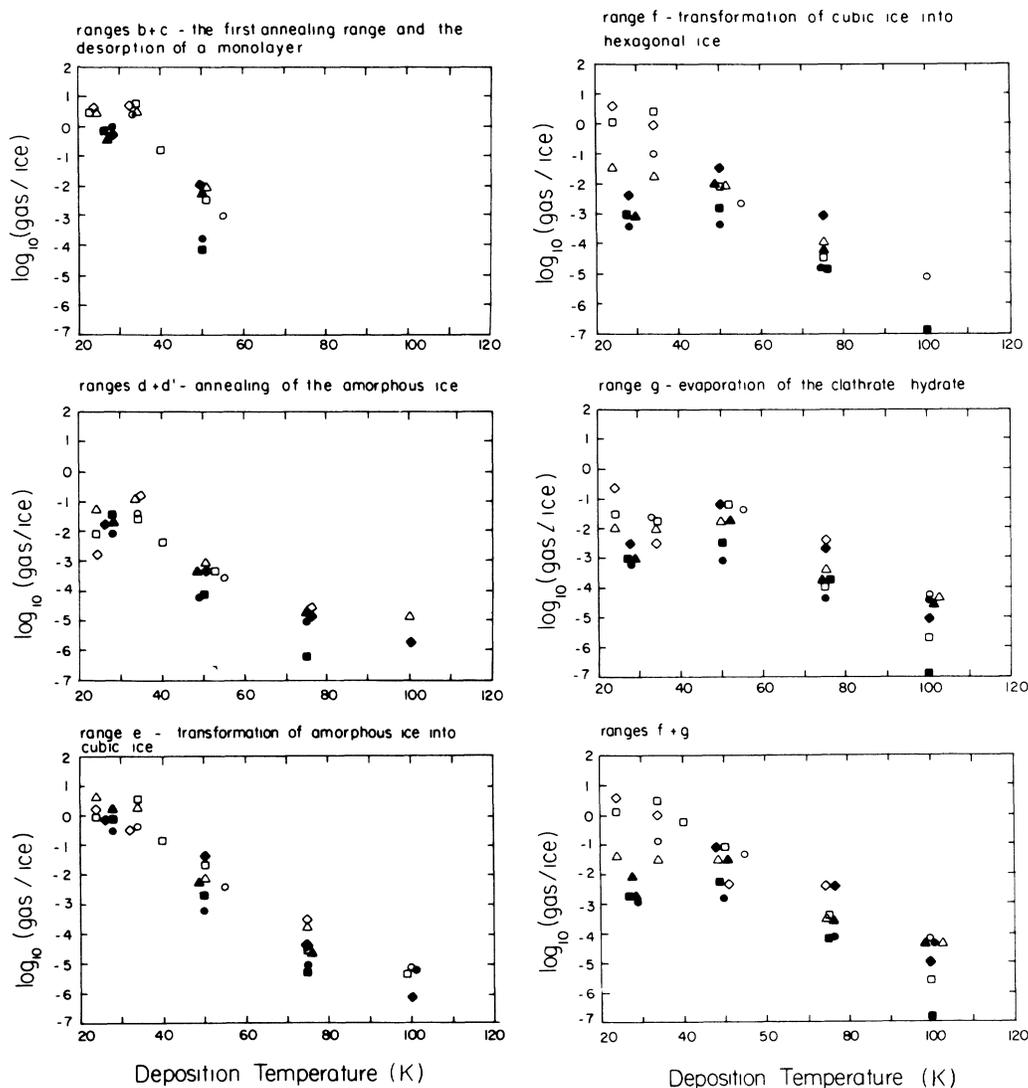
FIG. 3. The amounts of gases released in the various temperature ranges vs deposition temperature of the (water vapor) gas mixtures. $\Diamond$—CH_4, $\triangle$—CO, $\circ$—N_2 and $\square$—Ar. Open symbols represent the results of the deposition of 1:1 single gas-water vapor. Solid symbols represent the results of the deposition of gas mixtures $H_2O:CH_4:Ar:CO$(or N_2) = 1:0.33:0.33:0.33. Each point is an average of at least two experiments. (Some points were moved slightly on the temperature scale to prevent overlapping.)

(6) Hydrogen, diluting the (water vapor) gas mixtures by a factor of 35, did not affect the enhancements $CH_4 > CO > N_2 \gtrsim Ar$ or the amounts of these gases trapped in all the ranges between 35 and 100 K. The hydrogen itself was not trapped in the ice, since it is trapped only below 20 K.[3]

(7) Another group of experiments was carried out, in which $H_2O:CO:CH_4$ (1:1:0.01) or $H_2O:N_2$ (1:1) mixtures were deposited at 35 K and the ice was subsequently kept at 125 K for 21 h. This temperature is in the middle of the annealing of the amorphous ice in range (d'), just before the transformation into cubic ice, which commences at 137 K. During this long period, gas evolution dropped slowly to the detection limit—10^9 molecules sec^{-1}. However, when the heating was resumed, a mere increase of 2 K resulted in the resumption of gas evolution, at the flux which was obtained at 125 K before the prolonged heating. Thus, the gas does not leak from the annealing ice at 125 K during periods of the order of a day. When the gas-laden ice was kept for 21 h at 135–137 K, the temperature at which the amorphous ice transforms into cubic ice, most of the gas in ranges (e) and (f) leaked out, leaving in the ice only the gas trapped in range (g)—the clathrate-hydrate. Apparently, the cubic ice was transformed to hexagonal ice during 21 h at 136–137 K, but the clathrate-hydrate was not affected. Schmitt et al.[8] did not observe this gas by its IR absorption, because their limit of detection was too high.[9]

IV. DISCUSSION

The picture of the amorphous ice which emerges from this study and our previous studies[1-3] is that of a needle-like solid, with a large surface area ($\sim$90 m^2 g^{-1}) and very high porosity. The pores might be looked at, as both microcracks and enlarged hexagonal channels in the not fully ordered amorphous ice, which close irreversibly during the stepwise, temperature dependent, annealing. The hexagonal channels reach their equilibrium dimensions during the transformations to cubic and hexagonal ice. If gas is trapped inside these microcracks and channels, their closure during the annealing and transformations squeezes some of the gas out, while locking the rest even more tightly, until further ordering in the ice releases it. All gas release proceeds via a mechanism of dynamic percolation, whereas a packet of gas escapes only when several channels open simultaneously into a channel leading to the surface.[3] The clathrate-hydrate cages open only when the ice evaporates, and only then can the enclathrated gas escape, together with the gas which was trapped in between the clathrate-hydrate crystallites. The clathrate-hydrates are probably formed around the walls of gas-filled channels, when the temperature is high enough ($\sim$45 K) to mobilize somewhat the rigid water molecules.[2]

At low temperatures (24–35 K), all four gases (CH_4, CO, N_2, and Ar) are trapped in the ice indiscriminantly, because their interaction with the water molecules surrounding them is more than sufficient to counteract their mobility. They are trapped in their proportion in the gas mixture also at 50 K, from a very gas-poor mixture [(wa-

ter vapor):gas = 100]. In this case, there are enough trapping sites in the ice and no competition is required among the various gases. However, in gas-rich mixtures [(water vapor):gas = 1] there is a severe competition among the various gases on the available trapping sites in the ice. Thus, at elevated temperatures (50–100 K), where both water molecules and gas atoms and molecules are more mobile, the interaction between the gas and the surrounding water molecules becomes increasingly important. The experimental results demonstrate that at and above 50 K the gases are trapped mainly in the clathrate-hydrate cages and in enclosed regions in the ice, which are opened only during the transformations into cubic (e) and hexagonal ice (f). The order of importance being (g) > (f) > (e), with an increased difference at the higher temperature (Figs. 2 and 3).

The degree of interaction of the gas atoms or molecules with the water molecules surrounding them is related to the energy of clathrate-hydrate formation for each gas. ΔH (water ice + gas → clathrate-hydrate) was calculated for CH_4, N_2, and Ar, to be -4.55, -3.81, and -2.94 kcal molecule^{-1}, respectively (e.g., Ref. 10). For the slightly dipolar CO, Davidson et al.[11] propose an interaction energy somewhat higher than for N_2. This degree of interaction seems to affect the trapping of gas in all three ranges [(e), (f), and (g)], since in all three of them the relation $CH_4 > CO > N_2 \gtrsim Ar$ holds between 50 and 75 K.

However, the trapping efficiency for each gas under our experimental conditions cannot be related to ΔH in the usual exponential manner[12] since, at 50 K, this would invoke a CH_4/N_2 ratio of 1.67×10^3 and a CH_4/Ar ratio of 10^7, which are not observed experimentally. Hence, these ΔH values may serve as a mere indication to the trend in the gas trapping efficiency and other, probably kinetic and mechanistic factors should also be included. One such factor might be the size of the trapped atom and molecule, since they have to squeeze into the narrow microcracks and channels in the ice. Thus, the relatively small Ar atom has an advantage over the others, which offsets its relatively low interaction energy. An even clearer demonstration of the role of the size of the gas molecules was obtained by us from the trapping of H_2 and D_2 in ice at 18–20 K.[3] In this case, the narrow H_2 or D_2 molecules (2.2 Å wide) could permeate even crystalline ice, up to a gas-to-ice ratio of 0.63, by penetrating the 2.5-Å-wide hexagonal channels in cubic ice.

Another consideration which should be taken into account is the type of clathrate-hydrate formed. Both CH_4 and CO form a type-I clathrate, while N_2 and Ar form a type-II clathrate.[11] When the four gases interact simultaneously with the ice to form clathrate-hydrates, both type-I and type-II structures should be formed simultaneously, with some disruption of the long-range order in the ice. This might add to the enhancement in the trapping of CH_4 and CO over N_2 and Ar. However, this effect should be observed only in range (g)—the clathrate-hydrate, whereas ranges (e) and (f) also show the same enhancement: $CH_4 > CO > N_2 \gtrsim Ar$.

The competition between types I and II might still be

responsible for the very small amounts of trapped gas in (g) at low (24–35 K) temperatures: If the clathrate-hydrate is formed only at $T \geq 45$ K, where the gas and water molecules are mobile enough to form the clathrate cages,[2] a deposition below this temperature results in the filling in the channels in the ice with a mixture of all the gases indiscriminantly. When the ice is warmed to 45 K, both types of clathrates (I and II) have to be formed simultaneously and interfere with each other. Hence, the small amount of gas trapped in (g) at 24–35 K. With a single gas (Ar) where there is no competition on the formation of the clathrate, the sharp drop in (g) occurs only at 18–25 K. This, together with the similar drop in (f), which is not related to clathrate formation, show that this drop at low temperature has additional unknown reasons.

Moreover, while (f) and (g) decrease considerably at 24–35 K and even more so in a mixture of gases, (e) remain high and similar to the single gases. This might suggest that there are two different locations in the ice. The first traps gas which emerges in range (e), during the transformation of the amorphous ice into cubic ice, while the second traps gas which emerges during the transformation of the cubic ice into hexagonal ice (f) or forms a clathrate-hydrate (g). Each location or trapping mechanism is affected differently by a low temperature or a mixture of gases. Although we do not know how these locations differ from each other, it is clear that a gas molecule trapped at 24–35 K in the amorphous ice is already predestined at that time to emerge at different temperatures and by different changes in the ice. Apparently, it is predestined at that time to emerge in any of the eight different temperature ranges of gas evolution.

V. CONCLUSIONS

Whereas in our previous studies we assumed that the only factors influencing the trapping of gas in amorphous ice are the structure and dynamics of the ice, the present study shows that the gases themselves strongly influence this process.

The findings of this experimental study on the trapping of mixtures of CH_4, CO, N_2, and Ar in amorphous water ice at 24–100 K can be summarized as follows: At 24–35 K, all four gases are trapped indiscriminantly in the ice, mainly in ranges (b + c) and (e). They are trapped in the ice in their proportion in the gas mixture also at 50 K, from a water-rich mixture, when there are enough trapping sites and no competition is required.

However, in gas-rich mixtures (gas-water vapor = 1) at 50–75 K, there is a strong competition among the gases on the trapping sites in the ice, resulting in a clear enhancement in the order $CH_4 > CO > N_2 \gtrsim Ar$, in ranges (e), (f), and (g), which dominate the trapping. CH_4 and CO are trapped from a 1:0.33:0.33:0.33 $H_2O:CH_4:Ar:CO$ (or N_2 mixture to the same extent as when deposited alone, while the trapping of N_2 and Ar is suppressed by factors of 30 and 16, respectively. From a 1:1:0.01 $H_2O:CO:CH_4$ mixture, at 50 K, the CH_4 is trapped 40 times more efficiently than CO and, when the competition among the two is even stronger, when they are flowed into the amorphous ice rather than being codeposited with it, the CH_4 is trapped 150 times more efficiently than CO. This enhancement disappears altogether in gas-poor mixtures.

It seems that the order of enhancement in gas trapping $CH_4 > CO > N_2 \gtrsim Ar$ is determined by several factors: (1) The energy of interaction of the gas atoms or molecules with the water molecules surrounding them, in the channels of the amorphous ice; (2) the size of the gas atom or molecule, which enables it to enter narrower channels, and (3) the type of clathrate-hydrate formed (I or II). The same factors which determine the enhancement in clathrate-hydrate formation (g), also determine the enhancements in the trapping of these gases in channels in the amorphous ice, from which they emerge during the transformations of the amorphous ice to cubic ice (e) and hexagonal ice (f). The gas which is released during the annealing of the amorphous ice, in (b), (d), and (d'), is influenced by these factors to a much lesser degree. The gas is trapped in the amorphous ice in eight different locations, which are affected differently by the temperature or the gas mixture, and is predestined at the time of their trapping to emerge in a specific temperature range.

The combination of several factors severely limits a theoretical estimation of the relative trapping efficiencies of gases from a mixture and requires their experimental determination. This experimental data, combined with the recently acquired information on the gas composition of comet Halley, could give us an idea as to what might have been the gas composition of the solar nebula where, presumably, the coments were formed.[13]

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