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# NOTE

# Comments on "Gas Release from Comets" and Related Trapped-Gas Experiments

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**A recent paper on Kr trapping and release by $H_2O$ ice is used to emphasize the many variables that influence the results of trapped-gas experiments with cometary ice analogs. A proposed linear relationship between ice thickness and gas retained beyond the amorphous-to-cubic phase change of water is questioned. The many variables involved, combined with the uncertainty of cometary structure and composition, imply that great care is needed in the application of laboratory results to cometary phenomena and that definitive conclusions are difficult to reach.** © 1992 Academic Press, Inc.

Laboratory studies of cometary ice analogs have been published by several research groups in recent years (e.g., Moore *et al.* 1988, Sandford and Allamandola 1988, Schmitt *et al.* 1989, and Kouchi 1990). A typical experimental approach is to prepare a gas/water-vapor mixture, deposit it on a cold surface to form an amorphous-water ice, and then study the ice either by a spectroscopic or a diffraction method. This is often followed by warming the ice and observing its release of trapped gas as a function of temperature. These investigations of gas trapping and release and their cometary applications have gained considerable attention both from professional and from "popular" publications (e.g., *Sky & Telescope* 1988 and Greenberg 1984). With this in mind, this Note emphasizes the many variables in these experiments and the difficulty in comparing results, properly taking into account the variables involved.

The hazards of ignoring the many parameters in cometary ice experiments are illustrated by a recent paper of Notesco *et al.* (1991). The authors review work on $CO/H_2O$ ices from four research groups (Schmitt *et al.* 1989, Kouchi 1990, Sandford and Allamandola 1988, and Bar-Nun *et al.* 1987) and claim that an "apparent controversy" exists over CO trapped in ices warmed above ~135–150 K, the region of the amorphous-to-cubic phase change of $H_2O$ (region "e" of Notesco *et al.* (1991)). The authors go on to claim that the controversy "stems only from different thicknesses of the ice samples studied" and that a linear relationship exists between ice thickness and CO retention beyond ~135–150 K. While these claims might appear reasonable on a first reading of Notesco *et al.* (1991), careful examination shows that each is unfounded.

Of the four papers cited by Notesco *et al.*, each supposedly presenting a study of a $CO/H_2O$ ice with a certain thickness, one study actually concerned Ar, not CO (Bar-Nun *et al.* 1987).[1] Another paper (Schmitt *et al.* 1989) reported a range of ice thicknesses, not a single value as stated by Notesco *et al.* (1991).[2] This means that any controversy concerning CO trapping and ice thickness can only come from the work of Kouchi (1990) and Sandford and Allamandola (1988). While it is true that those two groups observed different CO trapping and release from $CO/H_2O$ ices, their choices of experimental conditions, not to mention the different methods used to study the ices, were not the same. Specifically, their initial (total CO)/(total $H_2O$) ratios differed by an order of magnitude, which is sufficient to account for any observed differences in CO release (Hudson and Donn 1991).[3] Thus, none of the four papers cited by Notesco *et al.* (1991) provide evidence of a controversy over CO trapping and release from $CO/H_2O$ ices above ~150 K.

Nevertheless, Notesco *et al.* (1991) present experiments to resolve the "apparent controversy" over CO retention in $CO/H_2O$ ices deposited at 10 K. Their experimental conditions are compared with those of other researchers in our Table I. The choice of Kr for the trapped gas and 48 K for the deposition temperature are surprising since it has been shown (Laufer *et al.* 1987) that both factors influence gas trapping. Although Notesco *et al.* cite another paper (Bar-Nun *et al.* 1988) as evidence that Kr is trapped and released in a way similar to CO, again inspection of the original paper shows otherwise; no work with $Kr/H_2O$ ices was

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[1] Our search of other papers (Bar-Nun *et al.* 1985, 1988, 1989 and Laufer *et al.* 1987) failed to uncover, $CO/H_2O$ experiments with ices ~3.4 $\mu$m thick, a density of 0.5 g cm$^{-3}$, and unequivocally reported to be made by codeposition.

[2] No special citation is given to indicate personal communication with Schmitt *et al.* concerning sample thickness. Our table gives values kindly supplied to us by Drs. Schmitt and Klinger.

[3] Bar-Nun *et al.* (1987) observed a similar effect with $Ar/H_2O$ ices.



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TABLE I
**Some Variables in Sublimation Experiments on Cometary Ice Analogs**

| Investigator(s) | Gas used | Sample deposit temp. (K) | Sample deposit rate ($\mu$m/hr) | Ice thickness ($\mu$) | Physical method(s) used[a] |
|---|---|---|---|---|---|
| Schmitt *et al.* (1989) | CO | 10 | 1–8[b] | 0.15–3.5[b] | IR |
| Kouchi (1990) | CO | 10 | 0.1 | 0.5 | ED/MS |
| Sandford and Allamandola (1988) | CO | 10 | 5 | 0.4 | IR |
| Notesco *et al.* (1991)[c] | Kr | 48 | 49–60 | 0.14–30 | MS |

[a] IR, infrared spectroscopy; ED, electron diffraction; MS, mass spectrometry.
[b] These values were kindly supplied to us in a personal communication from J. Klinger and B. Schmitt.
[c] Thickness calculated by Notesco et al. (1991) from an assumed sample density of 0.5 g cm$^{-3}$ in each case.

found in either the cited paper or others from the same group (Bar-Nun *et al.* 1985, 1989 and Laufer *et al.* 1987).

The deposition rates (i.e., growth rates of sample thickness) of 49–60 $\mu$m hr$^{-1}$ for the Kr/$H_2O$ experiments of Notesco *et al.* (1991) are also unusual. Their own table permits calculation of mass deposition rates, since deposit times and the corresponding number of $H_2O$ molecules in the ice are listed. The rates vary from 24 to 31 mg $H_2O$ hr$^{-1}$, high enough to cause concern about contamination of the amorphous ice by crystalline regions, especially at 48 K. (Narten *et al.* (1976) recommend rates under a few mg hr$^{-1}$ and temperatures under 55 K.) The table of Notesco *et al.* also shows deposit times spanning two orders of magnitude, raising concerns about structural variations from sample-to-sample due to thermal annealing (Bar-Nun *et al.* 1987), variations that could change each sample's ability to trap and retain Kr.

Notesco *et al.* (1991) also claim knowledge of ice thicknesses, although not through direct measurements. The total number of subliming $H_2O$ molecules was measured, an ice density of 0.5 g cm$^{-3}$ was assumed (according to the authors' Table), and then, presumably, a thickness was calculated from the cold finger's area (not given). Since the density is an assumption, a scaling problem remains for any astrophysical application. More fundamental is the question of whether a *constant, fixed* density applicable to all samples is consistent with ice thicknesses ranging over two orders of magnitude.

Perhaps most important is the (total Kr)/(total $H_2O$) ratios for the ices of Notesco *et al.* (their Figs. 1A–1D). The trapping and release of other gases (e.g., CO, $CO_2$, Ar) is known to be sensitive to this ratio (Hudson and Donn 1991, Sandford and Allamandola 1990, Kouchi 1990, Schmitt *et al.* 1989, and Bar-Nun *et al.* 1987) and so the same effect is expected with Kr. Unless this ratio is the same in all the Kr/$H_2O$ experiments of Notesco *et al.* (1991), interpretation of the experimental results becomes very difficult. Any attempt to observe and correlate gas trapping and release with ice thickness will be complicated by the influence of a varying (total Kr)/(total $H_2O$) ratio. Unfortunately, Notesco *et al.* did not state whether or not their ratio was constant.

The most obvious explanation for the results of Notesco *et al.* is that their ices had different (total Kr)/(total $H_2O$) ratios, although each ice was made from a gas-phase mixture with Kr/$H_2O$ = 0.1. Nonuniformity from sample-to-sample could arise from thermal annealing or partial crystallization due to the authors' choice of experimental conditions (i.e., deposit time, deposit temperature, deposit rate, and ice thickness). A time-dependent fractionation to give preferential deposition of $H_2O$ over Kr, decreasing the Kr/$H_2O$ ratio as the ice thickness increased, is also possible. It is perhaps significant that Hagen *et al.* (1981) found changes in ice homogeneity beyond a thickness of ~1.5 $\mu$m.

Even if these concerns over sample deposition temperature, deposition rate, ice thickness, the Kr/$H_2O$ ratio, and even the choice of Kr itself are ignored, an uncertainty remains as to what interpretation the authors are claiming for their results. In their abstract, their final paragraph, and the title of their table, Notesco *et al.* claim a relationship exists between the amount of gas retained by an ice beyond ~135–150 K and the ice's thickness, a relationship that would appear almost obvious. However, inspection of their text and table shows that it is not the *amount* of gas but rather the *concentration* of gas which is claimed as increasing with thickness. An intensive and an extensive property have been used interchangeably.

We briefly mention four other problems in the Note by Notesco *et al.* First, the authors never demonstrate how their work resolves the original "apparent controversy" described for CO/$H_2O$ ices. The CO trapping and release seen by Kouchi (1990) above ~135–150 K was smaller than that seen by Sandford and Allamandola (1988) who used a slightly thinner ice, a *contradiction* of the thickness dependence claimed by Notesco *et al.* in their abstract and final paragraph. Second, the linear effect claimed is based on four data points, two within experimental error,[4] a third quite close, and the fourth an order of magnitude different in ice thickness. Such data obviously appear linear whether they are or not. Third, the authors generalize their work to ices with thickness from 0.14 to 64 $\mu$m. In fact, the number of chemical constituents in their ices varied from two (0.14–30 $\mu$m thick Kr/$H_2O$ ices) to four (64 $\mu$m thick Kr/Xe/Ar/$H_2O$ ice) and the two thickest ices were subjected to a different thermal treatment than the others. Fourth, the interpolation in their final paragraph, using Table I to get the CO/$H_2O$ ratio in Comet Halley, is numerically incorrect. A linear least squares fit of the data gives CO/$H_2O$ = 0.22 or 18% CO.

We hope that by calling attention to the numerous parameters in trapped-gas experiments, and to some of their effects, that the confusion and ambiguities that otherwise follow in comparing different results can be avoided. An important consequence of all of this is the need to use great care in applying the results of laboratory ice sublimation experiments to cometary phenomena. In view of the many experimental variables and the uncertainties of cometary nuclear structure and composition, definitive conclusions about comets are very questionable.

*Added in revision.* A. Bar-Nun, as a referee of this Note, has informed us that the ices studied in Notesco *et al.* (1991) did *not* have the same (total Kr)/(total $H_2O$) ratio. Therefore both the ice thickness and the gas concentration were changing in the experiments presented. No conclusion about the role of thickness alone is possible. Moreover, with a varying concentration ratio, the density of the ice is also changing, making the assumption of a fixed density for all ices questionable. Unfortunately, this is precisely the assumption that was made since densities were needed to calculate ice thicknesses.

[4] Notesco *et al.* regard Kr/$H_2O$ values within a factor of 4 of one another as equal.

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