The Astrophysical Journal Letters, 784:L1 (4pp), 2014 March 20 doi:10.1088/2041-8205/784/1/L1

THE PHASES OF WATER ICE IN THE SOLAR NEBULA

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Received 2014 February 8; accepted 2014 February 12; published 2014 March 3

ABSTRACT

Understanding the phases of water ice that were present in the solar nebula has implications for understanding cometary and planetary compositions as well as the internal evolution of these bodies. Here we show that amorphous ice formed more readily than previously recognized, with formation at temperatures <70 K being possible under protoplanetary disk conditions. We further argue that photodesorption and freeze-out of water molecules near the surface layers of the solar nebula would have provided the conditions needed for amorphous ice to form. This processing would be a natural consequence of ice dynamics and would allow for the trapping of noble gases and other volatiles in water ice in the outer solar nebula.

Key words: planets and satellites: formation – protoplanetary disks – comets: general

Online-only material: color figure

1. INTRODUCTION

Whether water was present in the outer solar nebula as amorphous or crystalline ice remains a topic of debate. If amorphous ice formed in the nebula, then it would have been capable of trapping other gases present and could possibly explain the noble gas contents of comets and Jupiter (Bar-Nun et al. 1985; Owen et al. 1999; Yokochi et al. 2012). However, Kouchi et al. (1994) demonstrated that as water ice is expected to condense at temperatures of 120–180 K in the solar nebula, water molecules would have been able to arrange themselves into a crystalline structure. Because the D/H ratios of water throughout the solar nebula is significantly less than that found in the interstellar medium, it is thought that much of the ice in the nebula saw high temperatures near the young Sun then was carried outward to cooler regions, condensing at these temperatures along the way (Mousis et al. 2000; Yang et al. 2013). For example, bringing the D/H ratio of water from the interstellar ratio of ∼0.001–0.01 to the cometary values of 1.5–3 × 10^{-4} (Hartogh et al. 2011) requires that 70%–97% of water equilibrated with molecular hydrogen (solar D/H ∼ 10^{-5}) at high temperatures (>500 K) in the solar nebula, before cooling and condensing as ice. This has led many to argue that amorphous ice formation was precluded in the solar nebula, and that all water ice was crystalline requiring another means of trapping volatiles such as clathrates (Keller & Jorda 2001; Hersant et al. 2004).

The solar nebula is expected to have been a dynamic object, in which gas and dust were pushed around as mass and angular momentum were transported throughout the disk (Armitage 2011). As a consequence of this evolution, gas and dust would be transported throughout the disk and exposed to a variety of physical and chemical environments. Upon passing through such environments, the dust and gas could be altered by chemical reactions, irradiation, or phase transitions. This was demonstrated in Ciesla & Sandford (2012), as icy grains in the outer solar nebula were found to be lofted to high altitudes above the disk midplane and exposed to intense radiation fluxes which would break molecular bonds in the ices and allow the resulting ions and radicals to react to form more complex species. Thus just because a compound or phase is formed in a protoplanetary disk does not mean that original phase is preserved throughout the lifetime of the solar nebula.

In this Letter we revisit the conditions under which the various phases of water ice would form in the solar nebula. In particular, the conditions for amorphous ice formation in the solar nebula are derived assuming that the ice forms on a substrate other than hexagonally crystalline ice. We then show that the conditions for amorphous ice formation would have been met as icy grains were irradiated by UV photons at the surface layers of the solar nebula and the resulting photodesorbed water froze out again at greater depths inside the protoplanetary disk.

2. FORMATION CONDITIONS OF ICE PHASES

Kouchi et al. (1994) determined that the phase of water ice that forms during condensation is controlled by the ability of condensing water molecules to rearrange themselves on the surface of the substrate. That is, if water molecules condense at some flux below a critical value, $F < F_c$, the water molecules are able to diffuse across the surface and achieve a minimum energy state, thus forming crystalline ice. At higher fluxes, $F > F_c$, the delivery of water molecules to the surface is so rapid that they cannot rearrange themselves into an ordered state before being locked into place. This results in the formation of amorphous ice. A key factor in setting F_c is the surface diffusivity of the substrate the water ice lands on: for high surface diffusivity, water molecules can readily rearrange themselves and form crystalline ice, while lower surface diffusivities lead to the formation of amorphous ice. As surface diffusivity is temperature dependent, amorphous ice is most easily formed at low temperatures.

Using the surface diffusion for hexagonally crystalline water ice (I_h), Kouchi et al. (1994) found that throughout the solar nebula, all water would have frozen out at fluxes that were orders of magnitude below F_c (=D/a^4, where D is the surface diffusivity of the substrate and $a = 4.5 \times 10^{-8}$ cm is the lattice constant of crystalline ice), and thus concluded that all water ice in the solar nebula would be crystalline. I_h has a relatively high surface diffusivity ($D_h = 0.045 \exp(-1230/T)$ cm^2 s^{-1}) for ice. However, in that same study, the authors experimentally determined the surface diffusivity for polycrystalline or cubic crystalline ice (represented by I_p here, but often seen as I_c—we avoid using the subscript c to avoid confusion when talking about F_c) a phase whose discontinuities in its crystal lattice and uneven surface leads to low surface diffusion rates

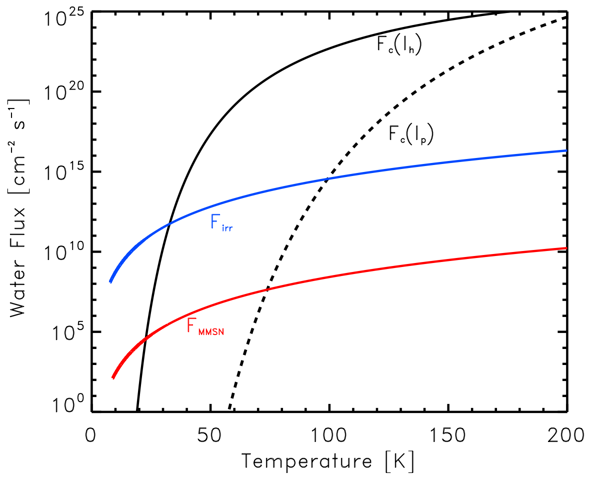

Figure 1. Black lines show the critical flux (F_c) for amorphous ice formation vs. temperature for a substrate of hexagonal ice (I_h, solid) and polycrystalline ice (I_p, dashed) from Kouchi et al. (1994). The flux of condensing water at the disk midplane for a minimum mass solar nebula (MMSN, red) and for an irradiated disk with surface density $\Sigma = 2000(r/1\ \mathrm{AU})^{-1}$ g cm^{-2} (irr, blue) are also shown.

(A color version of this figure is available in the online journal.)

($D_p = 1.74 \times 10^5 \exp(-4590/T)$ cm^2 s^{-1}; Kouchi et al. 1994). I_p will form at temperatures $< \sim$200 K as a metastable phase, whereas I_h will be the crystalline form at higher temperatures (Baragiola 2003; Hobbs 2010). As water ice would have formed in the solar nebula at temperatures between 120 and 180 K (depending on ambient pressure) water ice initially would have been in the form of I_p rather than I_h.

Figure 1 compares the values of F_c for the case of water condensing onto I_h as done by Kouchi et al. (1994) and onto I_p using the parameters for polycrystalline ice derived from the experiments in that same paper. These fluxes are plotted as functions of temperature. For reference, the condensing flux of water vapor in a minimum mass solar nebula (MMSN; Weidenschilling 1977; Hayashi 1981) and a disk with a surface density of $\Sigma(r) = 2000(r/1\ \mathrm{AU})^{-1}$ and $T(r) = 150(r/1\ \mathrm{AU})^{-(3/7)}$ which represents a slightly more massive, irradiated disk (Chiang & Goldreich 1997) are shown. For both disks, the condensing flux is calculated at the disk midplane for the corresponding temperatures, where the flux would be greatest, assuming all water is present as a vapor.

As can be seen, F_c is orders of magnitude higher for I_h than I_p at all temperatures relevant to the solar nebula. Whereas F_c would have reached low enough values to allow amorphous ice to form at temperatures <20 K in the solar nebula based on the Kouchi et al. (1994) calculations, amorphous ice may be able to form at temperatures of 70–90 K if one accounts for the fact that I_p is likely the original phase for water ice in the disk.

3. ICE FORMATION CONDITIONS IN THE SOLAR NEBULA

While amorphous ice may be able to form at higher temperatures than originally calculated by Kouchi et al. (1994), these temperatures are still significantly below the temperatures where water ice is expected to condense under solar nebula temperatures. That is, as a gas of solar composition cools, or as a parcel of material migrates outward from the inner regions of the solar nebula, water ice forms at temperatures in the 120–180 K range, leaving negligible water in the vapor phase to condense at lower temperatures where amorphous ice would be expected.

However, a reservoir of cold water vapor has recently been detected in the protoplanetary disk around TW Hydrae by the *Herschel Space Observatory* (Hogerheijde et al. 2011). This water vapor is inferred to be present at the disk surface, with most of the observed emission lines originating 100–200 AU from the central star, where temperatures are <50 K. As thermal desorption would be minimal here, the water vapor is believed to result from the UV photodesorption of water ice covered grains at the disk surface, where 1 out of every ∼1000 incident photons liberates a water molecule (net yield $Y = 0.001$; Öberg et al. 2009). Water molecules liberated in this way, however, would not remain in the gas phase, and would freeze out again at the low temperatures found in the disk in this region, if they are not photodissociated themselves, as we discuss further below.

To explore how much water would be liberated and freeze out again in this manner, we consider the distribution of water vapor in a column of a protoplanetary disk at $r = 30$ AU, with a surface density of 60 g cm^{-2} and a temperature of 20 K (values close to the irradiated disk considered above). Such values would be expected for a typical T Tauri disk. We take the column to be isothermal; while disk surface layers may reach higher temperatures due to direct irradiation from the central star, the temperatures expected there would be 30–50 K, still below the temperatures where thermal desorption is important and thus these temperature variations are not important for our purposes. We consider dust grains to be uniformly distributed throughout the column with an average radius of $a = 1\ \mu$m. Assuming a grain density of $\rho_g = 2$ g cm^{-3} and dust-to-gas mass ratio of 0.01, the opacity of the column is $\kappa = 37.5$ cm^2 g^{-1}.

The freeze-out flux of water vapor would be given by $F_{\mathrm{FO}} = n_{\mathrm{H_2O}} v_{\mathrm{th}}$, where $n_{\mathrm{H_2O}}$ is the ambient density of water molecules and v_{th} the thermal velocity of the water molecules. The photodesorption flux would be given by $F_{\mathrm{PD}} = G_0 10^8 Y e^{-\tau}$, where 10^8 is the flux of UV in the interstellar radiation field (in cm^{-2} s^{-1}; Habing 1968), G_0 is a factor which measures how much stronger the incident UV radiation field is than the interstellar field, and τ is the optical depth into the disk of the region of interest. The net flux $F_{\mathrm{net}} = F_{\mathrm{PD}} - F_{\mathrm{FO}}$ will be positive, meaning water molecules will be lost from the grains and added to the vapor in the upper regions of the disk where UV fluxes are high (optical depths are low). Freeze-out and ice formation will occur when $F_{\mathrm{net}} < 0$ deeper in the disk. Thus the flux at which water is delivered to the surface of a grain in this situation will depend on the time it takes for grains and vapor to migrate from the UV irradiated layer to the shielded disk interior.

To estimate the typical time for such migration and the corresponding fluxes of water from and onto the grains, the particle tracking methods of Ciesla (2010) were used to track how parcels of materials would migrate through the vertical column of the disk considered here. The path of a typical parcel is shown in Figure 2 over a 10^5 yr time period. For the sake of our calculations, we consider the case of the disk with an incident flux of $G_0 = 10^4$ at 30 AU, which is a typical value for a T Tauri star due to the accretion of mass onto the young star (Bergin et al. 2004). The radiation was assumed to propagate perpendicular to the disk for simplicity—in reality, the radiation from the central star will be incident at some angle, limiting the depth of penetration to less than that found here. We simulated this effect by increasing the opacity of the column by factors of 5–10, such that the UV dominated region is limited to the very upper surface layers of the disk and found this to have no major

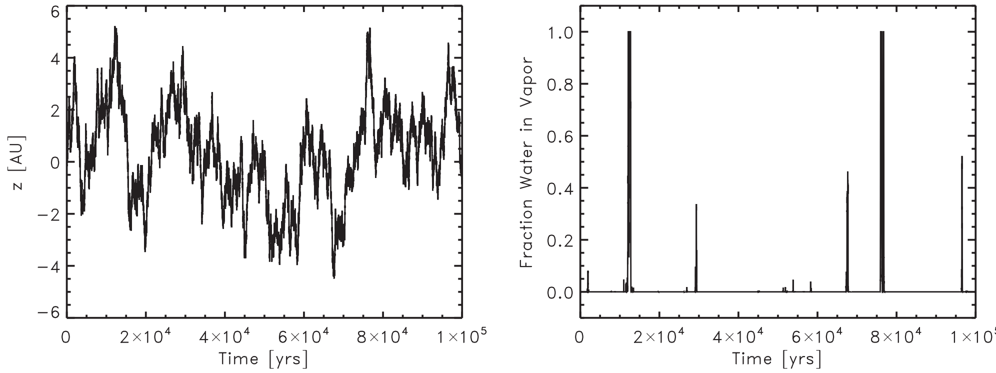

Figure 2. Left: typical vertical path of a parcel of solar nebula materials at $r = 30$ AU. Right: the fraction of water residing in the vapor phase for the particle shown on the left. Note the greatest fraction of water in the vapor corresponds to times when the particle is lofted to very high altitudes. Residence in the photodesorption region ranges from less than 0.1 to a few years.

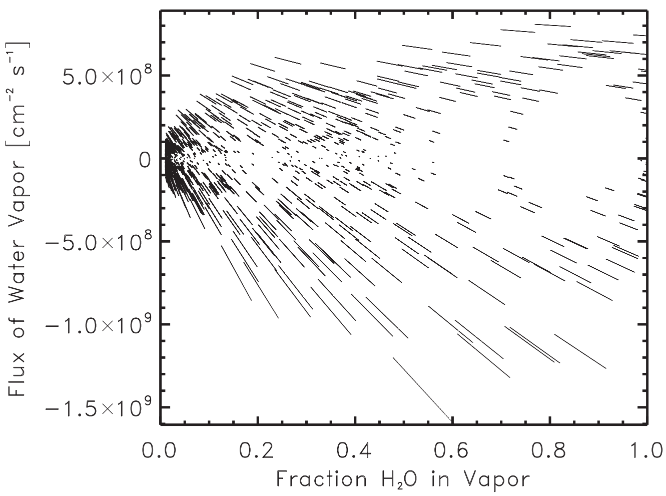

Figure 3. Flux of water vapor for the parcel of material whose path is shown in Figure 2 as a function of the amount of water found in the vapor. Negative fluxes indicate freeze-out of water. Freeze-out fluxes are in the range $\sim 10^5$–10^9 cm^{-2} s^{-1} when many of the water molecules have been removed from the grains.

effect on our conclusions. A turbulent parameter of $\alpha = 10^{-2}$ was assumed.

The net flux of water to/from the grain surface along the path was found by calculating the net flux as described above at each point along the trajectory of the materials considered, with solid particles and water vapor comoving. All particles began at the disk midplane with all water condensed on their surfaces (H_2O/H_2 abundance ratio of 2×10^{-4} was used here—uncertainties in this ratio are likely on the order of a few, and thus have a small impact on our results). This net flux is plotted as a function of the amount of vapor residing in the gas in Figure 3. The positive fluxes correspond to times when photodesorption dominates, leading to water molecules being incorporated into the gas. As the grain and vapor migrate deeper into the disk, the flux is negative, meaning ice formation occurs. The magnitude of fluxes at which this ice forms takes place range from $\sim 10^5$ to 10^9 molecules cm^{-2} s^{-1} when more than 10% of the water has been photodesorbed. These fluxes exceed F_c in Figure 1 by orders of magnitude for both the case of ice formation on I_h and I_p at the 20 K temperature considered here. The same calculation was repeated for multiple particles and at temperatures ranging from 10 to 50 K. In all cases grains were found to reach altitudes where they would lose all of their water due to photodesorption and then see water ice reform at fluxes that exceeded $F_c(I_p)$, while $F_c(I_h)$ was even exceeded at low (<20 K) temperatures. As such fluxes were achieved at higher temperatures, this indicates that the warmer temperatures at higher altitudes would still allow amorphous ice to form. Thus the water vapor would freeze out as it moved to lower heights in the disk as amorphous ice, allowing water that began as crystalline ice to be transformed to amorphous ice by the cycling described here.

4. DISCUSSION

The results presented here show that even if water ice condensed in the solar nebula at temperatures in the 120–180 K range, where crystalline ice is expected to form, the dynamical evolution of the icy grains in the outer solar nebula would lead this ice to be lost and reformed as amorphous ice. Formation of amorphous ice in this manner may allow for the trapping of other gaseous species, such as N- and C-bearing species as well as noble gases. The trapping of such species in ices would allow volatile-rich planetesimals to form in the outer nebula, and may explain the enhanced abundances of these elements relative to hydrogen in the Jovian atmosphere compared to a gas of solar composition (Owen et al. 1999; Atreya et al. 2003).

An issue that requires further attention is the detailed fate of the liberated water at the upper layers of the protoplanetary disk. If gas molecules are liberated sufficiently high in the disk, they may be photodissociated by the same UV photons that liberate them from the grains they are on. Indeed, while the surface regions of a protoplanetary disk will have a molecular layer where molecules are stable underneath an atom-dominated region, where the atoms are produced by the dissociation of molecules. Taking an upper limit of $n_{H_2O}/n_H \sim 2 \times 10^{-7}$, which is estimated in irradiated regions of disks under steady-state conditions with no dynamic transport (Hollenbach et al. 2009), would give fluxes that would be at worst 1000 times smaller than those presented here. These values still exceed the $F_c(I_p)$ (Figure 1) for temperatures <60 K by orders of magnitude, meaning amorphous ice would still form. The extent to which materials are photodissociated will depend on the extent of time materials spend in the extreme upper layers of the disk. As shown here, the amount of water surrounding a grain will constantly be changing, with molecules freezing out and then being liberated over and over again. Thus there will be a time component to determining the precise fraction of water molecules that are liberated around particular grains that gets photodissociated compared to the bulk water present in a given region. This will be the focus of future work. Even if dissociation is important, the resulting species will freeze out again and reform H_2O again on grain surfaces at very rapid rates (Ioppolo et al. 2008; Dulieu et al. 2010). Given the low surface diffusivities of the molecules on I_c at the temperatures considered here, when such molecules form they would not be able to mobilize readily, resulting in amorphous ice.

The formation of amorphous ice alone would aid in the continued formation of this phase of water ice: the surface diffusivity of amorphous ice is orders of magnitude smaller than I_c (Kouchi et al. 1994), meaning any water molecules formed or frozen out on it would remain locked in place and unable to rearrange into a crystalline structure. This would be true whether the amorphous ice formed via direct freeze-out, surface processes, or through irradiation damage. Leto & Baratta (2003) found that crystalline water ice would be amorphized after receiving a dose of UV photons of a few eV per molecule, or a few UV photons per molecule. The dosages calculated here are beyond those needed for amorphization. Thus any water ice the forms as a result of photodesorption in the outer solar nebula is likely to be amorphous.

Should we thus expect all water ice in the solar nebula and protoplanetary disks to become amorphous? Not necessarily. Just as we have shown that cycling of this type could lead crystalline ice to be transformed to amorphous ice, amorphous ice could be transformed to crystalline as it migrates through the protoplanetary disk. At temperatures near $\sim$100 K, amorphous ice undergoes a spontaneous phase transition, where molecules rearrange themselves to form crystalline ice. Thus as ice particles migrate radially in a protoplanetary disk and reach higher temperatures, the amorphous ice may be lost. Trapped volatiles that resided on the grain surface when ice molecules froze out on top of them may be retained, despite the phase transition (Viti et al. 2004; Collings et al. 2004), meaning that crystalline ices with trapped volatiles may also be present in such disks. Determining the relative abundances of each phase of ice requires a detailed investigation of the radial transport of icy grains throughout the evolution of the solar nebula, which should be the goal of future work.

F.J.C. is grateful for stimulating and insightful discussions with Ted Bergin and Reika Yokochi. This work was supported by grants NNX11AK52G from the Origins of Solar Systems Program and NNX12AD59G from the Exobiology program.

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