

Note

On the possible noble gas deficiency of Pluto's atmosphere

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ABSTRACT

We use a statistical–thermodynamic model to investigate the formation and composition of noble-gas-rich clathrates on Pluto's surface. By considering an atmospheric composition close to that of today's Pluto and a broad range of surface pressures, we find that Ar, Kr and Xe can be efficiently trapped in clathrates if they formed at the surface, in a way similar to what has been proposed for Titan. The formation on Pluto of clathrates rich in noble gases could then induce a strong decrease in their atmospheric abundances relative to their initial values. A clathrate thickness of order of a few centimeters globally averaged on the planet is enough to trap all Ar, Kr and Xe if these noble gases were in protosolar proportions in Pluto's early atmosphere. Because atmospheric escape over an extended period of time (millions of years) should lead to a noble gas abundance that either remains constant or increases with time, we find that a potential depletion of Ar, Kr and Xe in the atmosphere would best be explained by their trapping in clathrates. A key observational test is the measurement of Ar since the Alice UV spectrometer aboard the New Horizons spacecraft will be sensitive enough to detect its abundance ~ 10 times smaller than in the case considered here.

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1. Introduction

Gas hydrates, or clathrates, may exist throughout the Solar System. Comparison of predicted stability fields of clathrates with conditions in various planetary environments suggest that these structures could be present in the Martian permafrost (Musselwhite and Lunine, 1995; Thomas et al., 2009; Swindle et al., 2009; Herri and Chassefière, 2012; Mousis et al., 2013), on the surface and in the interior of Titan (Tobie et al., 2006; Mousis and Schmitt, 2008), and in other icy satellites (Prieto-Ballesteros et al., 2005; Hand et al., 2006). It has also been suggested that the activity of many comets could result from the destabilization of these ices (Marboeuf et al., 2010, 2011, 2012a). On Earth, the destabilization of significant masses of CO₂ and CH₄ potentially stored in clathrates buried in seabeds and permafrost is regarded as a possible aggravating factor in future global warming (clathrate gun hypothesis – Kennett et al., 2003). Broadly speaking, clathrates

are thought to have taken part in the assemblage of the building blocks of many bodies of the Solar System and may be in other planetary systems (Lunine and Stevenson, 1985; Mousis et al., 2002, 2006, 2009, 2010, 2011, 2012a; Mousis and Gautier, 2004; Alibert et al., 2005; Marboeuf et al., 2008; Madhusudhan et al., 2011; Johnson et al., 2012).

Clathrates have also been proposed to be at the origin of the noble gas deficiency measured in situ by the Huygens probe in the atmosphere of Titan (Osegovic and Max, 2005; Thomas et al., 2007, 2008; Mousis et al., 2011). In the case of Mars, important quantities of argon, krypton and xenon are believed to be trapped in clathrates located in the near subsurface and their storage in these structures could explain the measured two order of magnitude drop between the noble gas atmospheric abundances in Earth and Mars (Mousis et al., 2012b). Here we investigate the possibility of formation of clathrates rich in noble gases on Pluto's surface. To do so, we use the same statistical–thermodynamic model applied to the case of Titan to determine the composition of clathrates that might form on Pluto and to investigate the possible consequences of their presence on the atmospheric composition.

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Table 1
Parameters for Kihara and Lennard-Jones potentials.

Molecule	σ_{K-W} (Å)	ϵ_{K-W}/k_B (K)	a_{K-W} (Å)	Reference
N ₂	3.0993	133.13	0.3526	Herri and Chassefière (2012)
Ar	2.9434	174.14	0.184	Herri and Chassefière (2012)
Kr	2.9739	198.34	0.230	Parrish and Prausnitz (1972)
Xe	3.32968	193.708	0.2357	Sloan and Koh (2008)

σ_{K-W} is the Lennard-Jones diameter, ϵ_{K-W} is the depth of the potential well, and a_{K-W} is the radius of the impenetrable core, for the guest-water pairs.

Table 2
Parameters of the dissociation curves for various single guest clathrate hydrates. A is dimensionless and B is in K. Constants for Kr and Xe are given for an Arrhenius law making use of Napierian logarithm.

Molecule	A	B
N ₂	9.86	−728.58
Ar	9.34	−648.79
Kr	22.3934	−2237.82
Xe	16.62	−3159

Table 3
Assumed composition of Pluto's atmosphere at the ground level. Noble gas abundances relative to N₂ are assumed to be protosolar (Asplund et al., 2009).

Species, K	Mole fraction, x_K
N ₂	9.31×10^{-1}
Ar	6.92×10^{-2}
Kr	4.90×10^{-5}
Xe	4.79×10^{-6}

2. The statistical–thermodynamic model

To calculate the relative abundances of guest species incorporated in a multiple guest clathrate (hereafter MG clathrate) at given temperature and pressure, we use a model applying classical statistical mechanics that relates the macroscopic thermodynamic properties of clathrates to the molecular structure and interaction energies (van der Waals and Platteeuw, 1959; Lunine and Stevenson, 1985). It is based on the original ideas of van der Waals and Platteeuw for clathrate formation, which assume that trapping of guest molecules into cages corresponds to the three-dimensional generalization of ideal localized adsorption.

In this formalism, the fractional occupancy of a guest molecule K for a given type t (t = small or large) of cage (see Sloan, 1998; Sloan and Koh, 2008) can be written as

$$y_{K,t} = \frac{C_{K,t} P_K}{1 + \sum_j C_{j,t} P_j}, \quad (1)$$

where the sum in the denominator includes all the species which are present in the initial gas phase. $C_{K,t}$ is the Langmuir constant of species K in the cage of type t , and P_K is the partial pressure of species K. This partial pressure is given by $P_K = x_K \times P$ (we assume that the sample behaves as an ideal gas), with x_K the mole fraction of species K in the initial gas, and P the total atmospheric gas pressure, which is dominated by N₂. The Langmuir constant depends on the strength of the interaction between each guest species and each type of cage, and can be determined by integrating the molecular potential within the cavity as

$$C_{K,t} = \frac{4\pi}{k_B T} \int_0^{R_c} \exp\left(-\frac{w_{K,t}(r)}{k_B T}\right) r^2 dr, \quad (2)$$

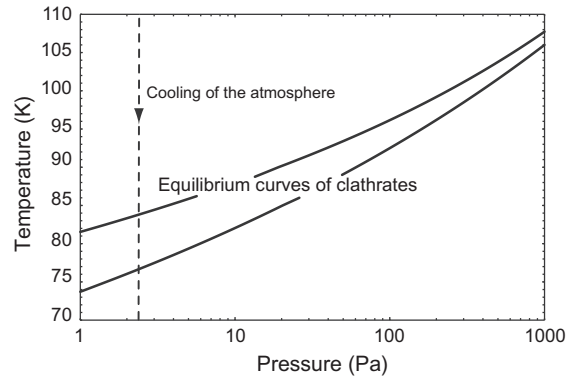


Fig. 1. From top to bottom: equilibrium curves of Xe-, Kr-, and Ar-dominated clathrates (the latter two appear superimposed). The arrow pointing down represents the path followed by a cooling atmosphere with a surface pressure of 2.4 Pa. When the cooling curve intercepts an equilibrium curve, then the corresponding clathrate forms.

where R_c represents the radius of the cavity assumed to be spherical, k_B the Boltzmann constant, and $w_{K,t}(r)$ is the spherically averaged Kihara potential representing the interactions between the guest molecules K and the H₂O molecules forming the surrounding cage t . This potential $w(r)$ can be written for a spherical guest molecule, as (McKoy and Sinanoğlu, 1963)

$$w(r) = 2z\epsilon \left[\frac{\sigma^{12}}{R_c^{11} r} \left(\delta^{10}(r) + \frac{a}{R_c} \delta^{11}(r) \right) - \frac{\sigma^6}{R_c^5 r} \left(\delta^4(r) + \frac{a}{R_c} \delta^5(r) \right) \right], \quad (3)$$

with

$$\delta^N(r) = \frac{1}{N} \left[\left(1 - \frac{r}{R_c} - \frac{a}{R_c} \right)^{-N} - \left(1 + \frac{r}{R_c} - \frac{a}{R_c} \right)^{-N} \right]. \quad (4)$$

In Eq. (3), z is the coordination number of the cell. This parameter depends on the structure of the clathrate (I or II; see Sloan and Koh, 2008) and on the type of the cage (small or large). The Kihara parameters a , σ and ϵ for the molecule–water interactions, given in Table 1, have been taken from the recent compilation of Sloan and Koh (2008) when available and from Parrish and Prausnitz (1972) for the remaining species.

Finally, the mole fraction f_K of a guest molecule K in a clathrate can be calculated with respect to the whole set of species considered in the system as

$$f_K = \frac{b_s y_{K,s} + b_l y_{K,l}}{b_s \sum_j y_{j,s} + b_l \sum_j y_{j,l}}, \quad (5)$$

where b_s and b_l are the number of small and large cages per unit cell respectively, for the clathrate structure under consideration, and with $\sum_K f_K = 1$. Values of R_c , z , b_s and b_l are taken from Parrish and Prausnitz (1972).

In the present approach, the dissociation pressure of the MG clathrate and the mole fractions of the trapped volatiles are independently calculated. All mole fraction calculations are performed at the dissociation pressure $P = P_{mix}^{diss}$ of the clathrate, i.e. temperature and pressure conditions at which this ice forms. This dissociation pressure can be deduced from the dissociation pressure P_K^{diss} of a pure clathrate of species K, as (Hand et al., 2006; Thomas et al., 2007):

$$P_{mix}^{diss} = \left(\sum_K \frac{x_K}{P_K^{diss}} \right)^{-1}, \quad (6)$$

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