

**ON THE POSSIBLE NOBLE GAS IMPOVERISHMENT OF PLUTO'S ATMOSPHERE.** O. Mousis<sup>1,2</sup>, J. I. Lunine<sup>3</sup>, K. E. Mandt<sup>4</sup>, E. Schindhelm<sup>5</sup>, H. A. Weaver<sup>6</sup>, S. A. Stern<sup>5</sup>, J. H. Waite<sup>4</sup>, R. Gladstone<sup>4</sup> and A. Moudens<sup>7</sup>, <sup>1</sup>Université de Franche-Comté, Institut UTINAM, CNRS/INSU, UMR 6213, Besançon Cedex, France, [olivier.mousis@obs-besancon.fr](mailto:olivier.mousis@obs-besancon.fr), <sup>2</sup>Université de Toulouse; UPS-OMP; CNRS-INSU; IRAP; 14 Avenue Edouard Belin, 31400 Toulouse, France, <sup>3</sup>Center for Radiophysics and Space Research, Space Sciences Building Cornell University, Ithaca, NY 14853, USA, <sup>4</sup>Space Science and Engineering Division, Southwest Research Institute, San Antonio, TX 78228, USA, <sup>5</sup>Southwest Research Institute, 1050 Walnut Street, Boulder, CO 8030223, USA, <sup>6</sup>Space Department, Johns Hopkins University Applied Physics Laboratory, 11100 Johns Hopkins Road, Laurel, MD 20723-6099, USA, <sup>7</sup>LERMA, Université de Cergy-Pontoise, Observatoire de Paris, ENS, UPMC, UMR 8112 du CNRS, 5 mail Gay Lussac, 95000 Cergy Pontoise Cedex, France.

**Introduction:** 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 [1–4], on the surface and in the interior of Titan [5,6], and in other icy satellites [7,8]. It has also been suggested that the activity of many comets could result from the destabilization of these ices [9–11]. On Earth, the destabilization of significant masses of CO<sub>2</sub> and CH<sub>4</sub> potentially stored in clathrates buried in seabeds and permafrost is regarded as a possible aggravating factor in future global warming (clathrate gun hypothesis [12]). 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 [13–24]. 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 [25,18]. 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 [26].

Here we investigate the possibility of formation of clathrates rich in noble gases on Pluto's surface. To do so, we use a statistical-thermodynamic model in order to determine the composition of clathrates that might form on Pluto. 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 at a pressure range between 1 and 10<sup>3</sup> Pa. The formation of noble gas-rich clathrates on Pluto could then induce a strong decrease of their initial atmospheric abundances.

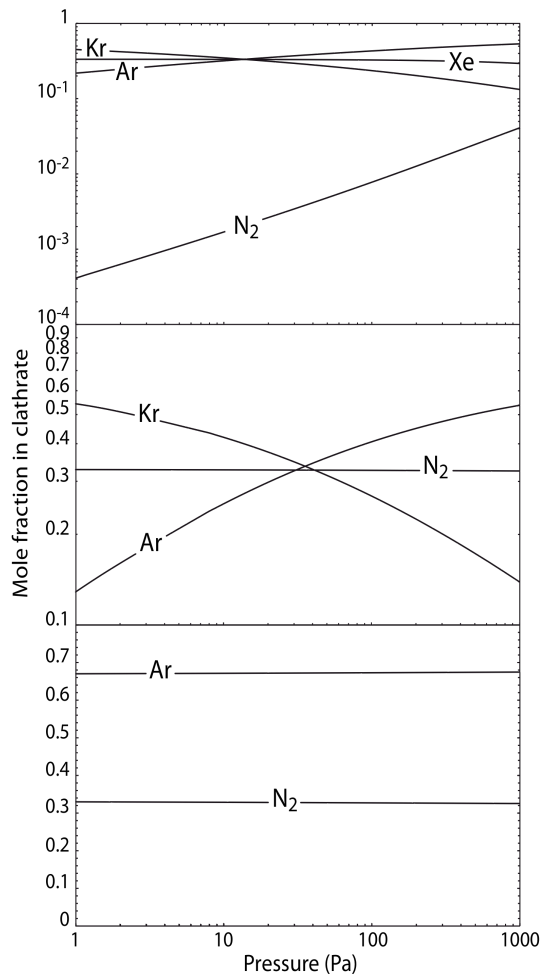
**The statistical-thermodynamic model:** To calculate the relative abundances of guest species incorporated in a multiple guest clathrate (hereafter MG clathrate) at given temperature and pressure, we use a model applying classical statistical mechanics that re-

lates the macroscopic thermodynamic properties of clathrates to the molecular structure and interaction energies [27, 13]. 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.

**Results:** We made the conservative assumption that all noble gases were initially present in the proto-atmosphere of Pluto, with Ar/N, Kr/N and Xe/N ratios assumed to be protosolar. Because Pluto's proto-atmosphere is expected to be strongly dominated by N<sub>2</sub> and that N<sub>2</sub> clathrate is of structure II [13], we present here calculations of the MG clathrate composition only for this structure.

From our calculations, we find that three successive layers of clathrates might form on Pluto's surface, each of them containing noble gases in different proportions. Figure 1 shows the composition of these clathrate layers computed for an atmospheric pressure ranging between 1 and 10<sup>3</sup> Pa. A first layer forms from the initial atmospheric composition. Irrespective of the pressure considered, the mole fraction of Xe trapped in this clathrate is ~0.3, i.e. a value that is ~63,000 times larger than its atmospheric mole fraction. The mole fraction of Kr is also strongly enhanced by a factor of ~4,800-9,600 compared to its atmospheric value and that of Ar is moderately enriched by a factor of ~3-6 times compared to its atmospheric value. The second clathrate layer forms once Xe is fully trapped in the first layer. In this case, only N<sub>2</sub>, Kr and Ar remain in the gas phase (the mole fractions of these species trapped in the first layer remain negligible). The mole fraction of Kr trapped in this clathrate is enhanced by a factor of 2,800-10,700 times compared to its atmospheric mole fraction in the 1-10<sup>3</sup> Pa pressure range. The Ar mole fraction in this layer is also found to be moderately enriched by a factor of ~2-8, compared to its atmospheric mole fraction. In its turn, a third clathrate layer forms when Kr is fully trapped in the second layer and in this case only N<sub>2</sub> and Ar remain in the coexisting gas phase. The fraction of Ar trapped in this clathrate remains constant irrespective of the surface

pressure considered and is found to be  $\sim 10$  times larger than its atmospheric value.



**Figure 1:** Mole fractions of volatiles encaged in clathrates and calculated as a function of the surface pressure of N<sub>2</sub>. Noble gas abundances are assumed to be protosolar relative to N<sub>2</sub>. The clathrate composition is investigated from a gas phase composed of Ar, Kr and N<sub>2</sub> (top panel), of Ar, Kr and N<sub>2</sub> (middle panel), and of Ar and N<sub>2</sub> (bottom panel).

If Ar, Kr and Xe were initially in protosolar abundances in the atmosphere of Pluto, the amount of clathrates needed for their sequestration is relatively low. For example, if the three clathrate layers formed at their equilibrium temperatures (the equilibrium temperatures of the first, second and third clathrate layers are  $\sim 77$ ,  $76$  and  $76$  K, respectively). for a surface pressure of  $2.4$  Pa, their total equivalent thickness is of order  $10^{-3}$  m globally averaged on the planet, assuming a full clathration efficiency and the presence of a Structure II clathrate. Interestingly, calculations conducted in the case of formation of structure I clathrate

give comparable results in terms of noble gas trapping efficiencies and overall thickness of the clathrate layer.

A key observational test is the measurement of Ar since the Alice UV spectrometer aboard the New Horizons spacecraft [28] will be sensitive enough to detect its abundance  $\sim 10$  times smaller than in the case considered here.

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