THE TRAPPING OF Ar, Kr, AND Xe IN MARTIAN CLATHRATES AND THE POSSIBILITY OF DETECTING CLATHRATES ON MARS BY SEASONAL CHANGES IN THE Xe/Kr RATIO. T. D. Swindle[1], C. Thomas[2], O. Mousis[1,2], J. I. Lunine[1], and S. Picaud[2], [1]Lunar and Planetary Laboratory, University of Arizona, Tucson AZ 85721-0092 USA, [2]Université de Franche-Comté, Institut UTINAM, CNRS/INSU, UMR 6213, 25030 Besançon Cedex, France.

Summary: Calculations show that Xe would be much more readily trapped in multiple guest clathrates on Mars than would be Kr. Measurement of the Xe/Kr ratio over the course of a Martian year would be a sensitive detector of seasonal formation of clathrate.

Introduction: The existence of hydrate clathrates on Mars could be a substantial factor in the distribution and total inventory of that planet's volatiles. Clathrates have been discussed as a potential major reservoir for CO_2 [1], methane [2-4], and the noble gases krypton and xenon [5, 6]. Various authors have proposed that clathrates could be crucial for understanding Martian geomorphology [7-11], the presence and abundance of methane in the Martian atmosphere [2, 3], Mars' atmospheric history as deduced from noble gas outgassing [5, 12], and the abundance patterns of noble gases in Martian meteorites [6]. However, the thermodynamic stability field of clathrates is such that conditions on Mars are tantalizingly close to the stability boundary [13], so it is not known, and cannot be calculated a priori, whether clathrates are abundant, nonexistent, or something in between. Hence it is important both to determine what their effects might be, and to search for ways to test for their presence.

Calculations: To calculate the relative abundance of the different species incorporated in clathrate hydrates on Mars, we have used an approach based on the statistical model developed by van der Waals and Platteuw [14]. However, it differs from this latter approach by the use of experimentally determined dissociation curves in our code instead of calculated dissociation pressures [4, 15, 16]. This allows us to determine the relative abundances in clathrate hydrates down to very low temperatures whereas existing codes such as the CSMHYD program [17] are restricted to higher temperatures. Indeed, the dissociation pressure of the multiple guest clathrate in the CSMHYD program is calculated in an iterative way that requires the equality between the chemical potential in the clathrate phase and that in the gas phase. The determination of this equilibrium requires knowledge of the thermodynamics of an empty hydrate, such as the chemical potential, enthalpy and volume difference between ice (chosen as a reference state) and the empty hydrate. The experimental data available at standard conditions (T = 273.15 K, P = 1 atm) allow the CSMHYD program to calculate chemical potentials, and hence dissociation curves, as long as the temperature and pressure is not too far from the reference point. This method fails to converge at temperatures below 140 K

for the clathrates considered in this study. Our approach avoids this problem, because it uses experimentally determined dissociation curves, which are valid down to low temperatures. Our approach relies on four key assumptions: the host molecules contribution to the free energy is independent of the clathrate occupancy (this assumption implies in particular that the guest species do not distort the cages), the cages are singly occupied, there are no interactions between guest species in neighboring cages, and classical statistics is valid, i.e., quantum effects are negligible [17].

We considered a Martian atmosphere whose composition is dominated by CO_2, N_2, Ar, Kr, Xe, O_2 and CO, which derives from the data published by [18]. Moreover, since methane has recently been detected in the Martian atmosphere [19-21] and because its abundance might have varied over the ages, we consider initial gas phase abundances of CH_4 up to 1%, although it turned out the methane abundance had a very small effect on Kr and Xe.

For clathrate formation at a total pressure of 7 mbar, typical of the current Martian atmosphere, the relative abundance of Xe in the clathrate would be 33 times that the atmospheric Xe abundance, while that of Kr would be 0.57 times its atmospheric abundance. Argon is poorly incorporated into clathrates – its relative abundance in the clathrate would be less than 2% of its atmospheric abundance.

Discussion: The results provide support for previous suggestions that clathrates could be important reservoirs for the heavy noble gases, particularly Xe. For example, the Ar/Kr/Xe ratios in the present atmosphere might be a poor tracer of the primordial gas acquired [5], and the variations seen between the Xe/Kr ratios in "atmospheric" noble gas trapped in the shergottite Martian meteorites on the one hand, and the nakhlite meteorites and ALH84001 on the other, could be the result of changes in atmospheric Ar/Kr/Xe ratios because changes in the Martian climate led to formation or dissociation of clathrates [6].

A possibility that is testable in the near future is that clathrates form seasonally on Mars at present. The atmospheric pressure (basically the CO_2 pressure) is more than 30% higher at some parts of the Martian year than at others. If any substantial fraction of this seasonal variation is the result of formation/dissociation of clathrates, a large portion of Mars' current Xe inventory could be stored in clathrates during portions of the year. For example, if all of that 30% of the CO_2 were stored in clathrates, then (33 × 30%) = 990% times the minimum atmospheric abundance of Xe would be

stored there, which means the amount of Xe in the atmosphere would increase by roughly an order of magnitude from minimum CO_2 pressure to maximum. Even if only 10% of the CO_2 participating in the seasonal cycle went in and out of clathrates, the Xe abundance would change by roughly a factor of two.

Krypton, on the other hand, would only vary by 15% if all the seasonal CO_2 went into clathrates. Argon would change least of all the heavy noble gases, less than 1% even if all the seasonal change in pressure is from CO_2 incorporated into, and released from, clathrates.

Measuring absolute partial pressures of the noble gases may to be more difficult than measuring their ratios, so it is worth considering what would happen to ratios. Because Xe is enclathrated so much more effectively than Ar or Kr, the Xe/Kr or Xe/Ar ratio would change nearly as fast as the Xe abundance. Hence, the variability of the either the Xe/Kr or Xe/Ar ratio through the year would be a sensitive indicator of the presence of seasonal clathrates (Fig. 1). The Xe/Kr is an easier measurement target, since the ratio is of order unity, while Xe/Ar is of order 10^{-5}.

The Mars Science Laboratory is scheduled to launch in 2011, and the Sample Analysis at Mars (SAM) Instrument Suite includes a mass spectrometer which is designed to be capable of measuring Kr and Xe at the levels seen in the Martian atmosphere. Thus, SAM measurements through the course of the seasons should be able to set tight limits on the amount of clathrate formed seasonally.

This would not address the question of whether there are clathrates produced in other Martian climate regimes that are now buried, as has been suggested to explain Martian outflow channels, for example [9, 10]. However, this would provide some of the first real data about the presence or absence of clathrates on Mars.

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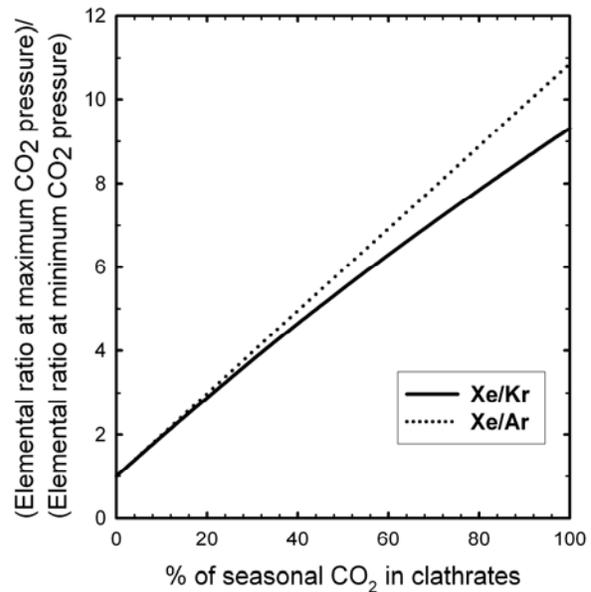[21] Mumma M. J. et al. (2008) in *American Astronomical Society DPS meeting #40*:. #6.05;

Fig. 1: Ratio of maximum to minimum Xe/Ar and Xe/Kr ratio as a function of the percentage of the seasonal CO_2 change that is due to clathrates. To read the graph, note that either elemental ratio would be unchanged through the year (maximum/minimum=1) if there is no clathrate (percentage = 0), and would increase to ~10 if all of the change in CO_2 pressure is from formation/dissociation of clathrate (percentage = 100).