CLATHRATE STORAGE OF VOLATILES ON MARS: Donald S. Musselwhite and Jonathan I. Lunine, Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ 85721

Introduction: The polar caps of Mars represent the largest known reservoir for volatiles on the surface of Mars. As such, any attempt to understand the volatile budget of the planet must take into account these vast deposits. The martian polar terrains consist of two components [1]: 1) Remnant ice caps which overlie 2) Polar layered deposits. Both types of units are characterized by deposits. The martian polar terrains consist of two components. Their age is less than 10^6 years [2]. The permanent north polar caps are H_2O ice I and dust. This conclusion is based on brightness temperatures and albedo measured in 1976 during Mars' north polar summer [3]. These observations are consistent with Mars Atmospheric Water Detector data for the northern hemisphere summer [4] which detected large amounts of water vapor over the north pole -- consistent with water ice in equilibrium with a water vapor saturated atmosphere.

The composition of the permanent south polar cap is not as clear-cut as that for the northern cap. Summer brightness temperatures, albedo and atmospheric water content are consistent with CO_2 at its sublimation point [5]. But an alternative possibility is H_2O+CO_2 clathrate being the main solid volatile phase. Miller and Smythe [6] proposed this idea on the basis of Mariner 7 data and phase stability experiments for CO_2 and H_2O. The temperature and pressure over the south pole in summer is within the stability field for H_2O+CO_2 clathrate in equilibrium with CO_2 vapor. In fact, under no conditions can solid CO_2 and H_2O ice coexist stably. The more recent Viking measurements discussed above are also consistent with H_2O+CO_2 clathrate being the main constituent of the south polar caps. The existence of H_2O+CO_2 clathrate at the south pole may explain the persistence of lower summertime temperatures above the caps compared with the north polar caps as H_2O+CO_2 clathrate has approximately one-fifth the heat conductivity of pure H_2O ice.

Storage of Trace Volatiles in the South Polar Caps: H_2O+CO_2 clathrate is a structure I clathrate with an ideal formula of CO_2·5.75 H_2O, although the actual formula is likely closer to CO_2·7 H_2O. It has two cage types -- the larger cage is made of 24 H_2O molecules, the smaller cage has 20 H_2O molecules. The CO_2 or other guest molecule fits within the cages. If the south polar caps are indeed H_2O+CO_2 clathrate, then they should have tremendous capacity for storing other volatile species such as noble gases.

To assess the storage capacity of H_2O+CO_2 clathrate under the conditions extant on Mars, we have calculated vapor/clathrate partitioning of noble gases, N_2 and CO using the equations developed by Lunine and Stevenson (1985). The abundance ratio of gas species k to l within the clathrate is given by the expression:

\[ f_{kl} = \frac{\{C_{1k} + P_l (1 + C_{2k} + P_k + C_{2k} + P_l) (1 + C_{2k} + P_k + C_{2k} + P_l) + 3 \cdot C_{2k} + P_k \}}{\{C_{1l} + P_k (1 + C_{2k} + P_k + C_{2k} + P_l) (1 + C_{2k} + P_k + C_{2k} + P_l) + 3 \cdot C_{2l} + P_l \}} \]

where: C = Langmuir Constant, P = Partial Pressure, subscripts 1 and 2 refer to sites 1 and 2 in the clathrate.

The abundance ratios for each trace gas species (Ne, Ar, Kr, Xe, N_2 and CO) to CO_2 stored within the clathrate were calculated individually. Langmuir constants are based on the method of [7]. The partial pressure of each species was determined from the volume mixing ratios [8] and the temperature was assumed to be 150°K. Since the Langmuir constants were not originally determined for this temperature, most of them had to be interpolated. The results of these calculations are shown in Figure 1, expressed as moles gas species to moles CO_2 along with the ratio of each gas species to CO_2 in the atmosphere. The concentrations of Kr and Xe relative to CO_2 exceed those in the atmosphere by several orders of magnitude. The concentrations of Ar, N_2 and CO are about 10% of their atmospheric values.

In order to determine the relative importance of the south polar cap as a reservoir for these various gas species vis a vis the atmosphere, we need to know the total volume of clathrate in the cap. The thickness of the cap plus layered deposits from Mariner 9 radio occultation data is one to two kilometers [1]. The caps themselves are likely no more than half of this. So an upper limit of one kilometer for the thickness of the H_2O+CO_2 clathrate is chosen. If the ice cap is much thinner than 10 meters, it probably would have visible bare spots in places. So an extreme lower limit of 10 meters for the thickness of the H_2O+CO_2 is chosen. The actual cap thick-
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ness is presumably somewhere between these two extremes. The concentration of each species in the clathrate was calculated assuming a ratio of $\text{H}_2\text{O}:\text{CO}_2 = 7:1$. Calculation of the total abundance of each gas species in the caps compared with the abundance of each species in the atmosphere is shown in Figure 2 for both the upper and lower limits for the cap thickness.

The simple but important lesson to be learned from this exercise comes in assessing the trace volatile budget of Mars based on measurements of the trace volatile abundances in the martian atmosphere. Since, if indeed the south polar cap of Mars is $\text{H}_2\text{O} + \text{CO}_2$ clathrate, then it also represents a more significant reservoir for Xe and possibly Kr than the atmosphere. Thus, the abundances of these gas species in the martian atmosphere are not representative of these abundances for the outgassed portion of Mars.

Figure 1:

*Figure 1: [Gases] in Atmosphere and Clathrate*

![Graph showing gases in atmosphere and clathrate]

Figure 2:

*Figure 2: Abundance in Clathrate/Atmosphere*

![Graph showing abundance in clathrate/atmosphere]

REFERENCES


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