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Storage of heavy noble gases into the Martian cryosphere

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Abstract

The difference between the measured atmospheric abundances of argon, krypton and xenon for Earth and Mars is striking. Because these abundances drop by at least two orders of magnitude as one moves outward from Earth to Mars, the study of the origin of this discrepancy is a key issue that must be explained if we are to fully understand the different delivery mechanisms of the volatiles accreted by the terrestrial planets. Here we aim to investigate whether it is possible to quantitatively explain the variation of the heavy noble gas abundances measured on Earth and Mars, assuming that these volatiles were sequestrated in the form of clathrates in the cryosphere of the ancient Mars. To do so, we use a statistical mechanical model to determine the composition of CO_2-dominated clathrates formed on the Martian surface in a pressure range between 0.007 and 3 bar at the ground level. We show that amounts of krypton and xenon equivalent to those found on Earth can be incorporated into the Martian cryosphere provided that the surface pressure exceeds $\sim$ 0.15 bar at their epoch of trapping into clathrates. In contrast, the incorporation of an amount of argon equivalent to the Earth value requires a surface pressure higher than $\sim$ 2.2 bar.

1 Introduction

Theories supporting the presence of clathrates on Mars initially focused on CO_2 as the sequestered gas, but have been extended to the investigation of the trapping of other gases. It was shown in 1970 that CO_2 clathrate is thermodynamically stable at the Martian poles [1]. Since then, many studies have postulated the existence of large CO_2 clathrate deposits both at the poles and in the subsurface at lower latitudes, and discussed their possible influence on the Martian climate or atmospheric composition [2, 3, 4]. Here we investigate the possibility that significant amounts of noble gases are sequestrated into the Martian cryosphere in the form of CO_2-dominated clathrates. In this scenario, these clathrates would have formed at early epochs on Mars during which the atmosphere was much denser than today.

2 Model

To calculate the relative abundances of guest species incorporated in Martian clathrates, we use a model applying classical statistical mechanics that relates the macroscopic thermodynamic properties of clathrates to the molecular structure and interaction energies [5, 6]. In this model, the relative abundance f_G of a guest species G in a clathrate (of structure I because CO_2 is the primary guest species) is defined as the ratio of the average number of guest molecules of species G in the clathrate over the average total number of incorporated molecules, as [5, 6]:

$$f_G = \frac{b_L y_{G,L} + b_S y_{G,S}}{b_L \sum_J y_{J,L} + b_S \sum_J y_{J,S}}, \quad (1)$$

where the sums in the denominator run over all species present in the system, and b_S and b_L are the number of small and large cages per unit cell, respectively. The occupancy fractions y_G of the guest species G for a given type of cage and for a given type of clathrate are determined from the Langmuir constants which are related to the strength of the interaction between each guest species and each type of cage. In a first approximation, this cage is assumed to be spherical and the corresponding interactions are represented by a spherically averaged Kihara potential, the integration of which within the cage giving the Langmuir constants [5, 6]. The calculation via Eq. 1 of the relative abundance of a guest species trapped in clathrate depend both on the structural characteristics of the considered clathrate and on the accuracy of the corresponding interactions between the trapped molecule and the water cage.

3 Results

Figure 1 shows the ratios of heavy noble gas abundances initially present in the Martian atmosphere and subsequently enclathrated into the cryosphere to the measured ones as a function of the surface pressure of CO_2 for three different cases of cage sizes. The figure shows that amounts of krypton and xenon (normalized in g/g-Planet) equivalent to those found on Earth can be incorporated into the Martian cryosphere provided that the surface pressure exceeds $\sim$ 0.15 bar at their epoch of trapping into clathrates. In contrast, the incorporation of an amount of argon equivalent to the Earth value requires a surface pressure higher than $\sim$ 2.2 bar.

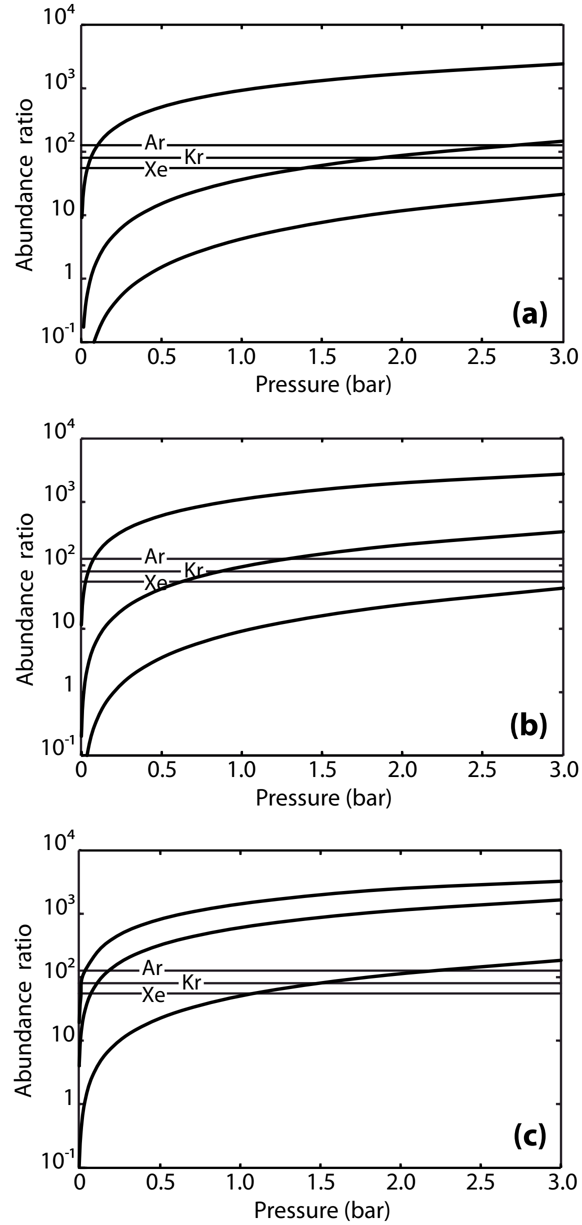

Figure 1: Ratios of heavy noble gas abundances initially present in the Martian atmosphere and subsequently enclathrated into the cryosphere to the measured ones represented as a function of the surface pressure of CO_2 in the cases of (a) a 2% increase of the cage sizes, (b) no cage variation and (c) a 2% contraction of the cage sizes. In each panel, abundance ratios plotted from top to bottom correspond to Xe, Kr and Ar, respectively. The three horizontal lines represent the ratios of measured heavy noble gas abundances (normalized in g/g-Planet) between the Earth and Mars.

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