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Isotopic fractionation through water vapor condensation: The Deuteropause, a cold trap for deuterium in the atmosphere of Mars

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Abstract. Recent observations of deuterium atoms at Lyman alpha with the Hubble Space Telescope have shown the puzzling result of a D/H ratio in the upper atmosphere of Mars to be 11 times smaller than the D/H ratio in HDO and H₂O of the lower atmosphere [Krasnopolsky *et al.*, 1998]. One factor to explain this vertical variation was proposed: the photo-induced fractionation effect (PHIFE), due to a lower absorption cross section of solar UV of HDO compared to H₂O [Cheng *et al.*, 1999]. Here we suggest that in addition to PHIFE, this vertical variation of D/H ratio is also the result of preferred condensation of HDO in rising air, a process already documented in the Earth's upper stratosphere. Results of a cloud model, including condensation, sedimentation, and sublimation of icy particles in the atmosphere of Mars, are presented, supporting the efficiency of the condensation/evaporation fractionation effect (CEFE) as an important factor controlling the D/H ratio in the upper atmosphere of Mars. For a typical H₂O profile, PHIFE provides a depletion factor of 2.5, while CEFE induces a factor of 3.5. The combined effects of PHIFE and CEFE (depletion factor of 9.5) can explain the paucity of D atoms in the upper atmosphere of Mars, implying a very low escape rate of deuterium at present and in the past and, correspondingly, a smaller quantity of H₂O in the past.

1. Introduction

The present atmosphere of Mars is thin, and its surface is too cold to allow liquid water. Still, the presence of ancient channels supports the belief that in the past, a warmer climate allowed running water, possibly life-sustaining. One clue to the Mars atmosphere evolution is the ratio of deuterated water vapor HDO to normal water vapor H₂O, measured to be (in the lower atmosphere) 6 times higher than on Earth. Because D atoms are twice heavier than H atoms, their escape rate from the top of atmosphere is much lower. Therefore it is believed that there has been in the past at least 6 times more H₂O on Mars than now (including the polar ice caps), depending on the ratio of escape rates of D and H, directly linked to the D/H ratio in the upper atmosphere.

The (D/H) ratio is 1.54×10^{-4} in the terrestrial oceans, while it is ~ 5.5 times larger in the water vapor phase of the atmosphere of Mars ($\text{HDO}/\text{H}_2\text{O} = 1.7 \times 10^{-3}$), as measured from IR absorption spectroscopy of solar reflected light in the lower atmosphere, where H₂O is mostly concentrated [Owen *et al.*, 1988; Bjoraker *et al.*, 1989; Krasnopolsky *et al.*, 1997]. Assuming that Earth's value was also the same for the early content of H₂O for Mars, the present Deuterium enrichment found (factor of 6) is due to preferential escape of H atoms from the top of the atmosphere. Therefore the total HDO remaining now in the planet is an indication of how much water the planet could have contained in the past.

If there never were any escape of D atoms, and only escape of H atoms, the extreme lower limit of past H₂O content is obtained by multiplying the current content (8–10 m) by this

enrichment ratio (here the current content is estimated from the volume of the north ice polar caps [Zuber *et al.*, 1998], if it were melted and spread over the whole planet; this known reservoir is able to exchange water with the atmosphere, while ice thought to be trapped in the permafrost is probably not able to exchange water and is therefore ignored here). Therefore the minimum value in the past would have been ~ 55 m (compared to 3 km for Earth).

On the other hand, if there was escape of D atoms together with H atoms, then H₂O content could have been much larger. Therefore the value of D atom escape rate is a crucial factor for the estimate of the H₂O past content. The estimate of escape mechanisms of D and H in the past must be extrapolated backward in time from our understanding of these mechanisms presently at work in the top of the atmosphere of Mars: either thermal escape or nonthermal escape. In both cases the escape rate of D atoms is proportional to the D number density in the upper atmosphere (altitude $z > 100$ km). It is possible to detect these D atoms with the Hubble Space Telescope (HST) from high-resolution spectroscopy, which is able to separate the Lyman α emissions of D and H atoms produced by resonance scattering of solar $\text{L}\alpha$ photons. An early attempt with HST [Bertaux *et al.*, 1992] gave a marginal detection of 30 rayleigh for the Martian D $\text{L}\alpha$ emission, while a second attempt with a better S/N ratio was more successful [Krasnopolsky *et al.*, 1998], revealing the D $\text{L}\alpha$ line at an intensity of 23 ± 6 rayleigh. The emission comes from altitudes larger than 100 km altitude, because of CO₂ absorption. This measured intensity implies the presence of HD molecules with a ratio $\text{HD}/\text{H}_2 = 1.5 \pm 0.6 \times 10^{-4}$, which is smaller by a factor 11 than the $\text{HDO}/\text{H}_2\text{O}$ ratio measured in the lower atmosphere at 1.7×10^{-3} . H₂O is the primary source of H and H₂, by a series of photochemical reactions, but the H that is seen at high alti-

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tudes ($z > 100$ km) comes exclusively from H_2 . The same is true for HDO, D, and HD.

The partitioning of D between HD and HDO in the atmosphere may be defined by $R = (\text{HD}/\text{H}_2)/(\text{HDO}/\text{H}_2\text{O})$. Surprisingly, the HST $\text{L}\alpha$ measurement of D atoms indicates a value of $R = 0.09$, much lower than the value $R = 1.6$ [Yung *et al.*, 1988] predicted by photochemical models (in which the reactions involving deuterated species are also included with different reaction rates).

The explanation proposed by Krasnopolsky *et al.* [1998] is that the HD concentration is not dictated by these reactions (kinetic control) but rather by isotopic exchange between H_2 and H_2O (thermodynamic equilibrium):



This explanation was rejected [Yung and Kass, 1998] on the grounds that it would require a rate coefficient of $10^{-23} \text{ cm}^6 \text{ s}^{-1}$, while laboratory measurements are only $10^{-33} \text{ cm}^6 \text{ s}^{-1}$. Therefore the conclusion of Yung and Kass [1998] is that either there is a hitherto unknown reaction that reduces the value of R in the photochemical models or there is a hitherto unknown catalyst on Mars which increases the efficiency of reaction (1) by 10 orders of magnitude. As quoted from Yung and Kass [1998, p. 1546]: “The resolution of this puzzle will be a major advance in our understanding of the evolution of the Martian atmosphere.”

Indeed, Cheng *et al.* [1999] recently proposed an elegant mechanism of differentiation, the photo-induced fractionation effect (PHIFE), because the HDO molecule is less prone to photodissociation than H_2O . Their UV absorption cross-section laboratory measurements for HDO are larger than for H_2O for $\lambda < 170$ nm and smaller for $\lambda > 170$ nm. For a typical temperature and H_2O vertical profile, Cheng *et al.* [1999] computed the photolysis rate (molecules $\text{cm}^{-3} \text{ s}^{-1}$) of H_2O and HDO as a function of altitude (assuming the two isotopomers have a similar mixing ratio vertical profile; see their Figure 2). This photolysis rate peaks around 25 km, because of the combination of decreasing solar UV absorbed by CO_2 and increasing concentrations of H_2O and HDO with decreasing altitude. Since CO_2 absorption screens out the solar UV spectrum below 170–180 nm at low altitudes where lies the bulk of H_2O and HDO, the net result is a smaller photodissociation rate for HDO than for H_2O . They computed that the vertically integrated photolysis rate (molecules $\text{cm}^{-2} \text{ s}^{-1}$) of HDO would be smaller than for H_2O by a factor ~ 2.5 (if their vertical mixing ratios were equal). However, they calculate that this depletion mechanism for the production of HD is still a factor of 3 too short to explain the low concentration of D atoms in the upper atmosphere as measured by HST [Krasnopolsky *et al.*, 1998].

2. Condensation/Evaporation Fractionation Effect

In fact, we suggest here a different explanation: the condensation/evaporation fractionation effect (CEFE), combined with the PHIFE effect, would most likely resolve the remaining differences in lower and upper atmospheric D/H ratios. When water vapor is condensing in the atmosphere to form icy grains, HDO is known to condense more easily than H_2O . Then these icy grains would fall under gravity and resublimates at lower altitude. This process would deplete the quantity of HDO in the vapor phase of the air parcel rising at altitudes where

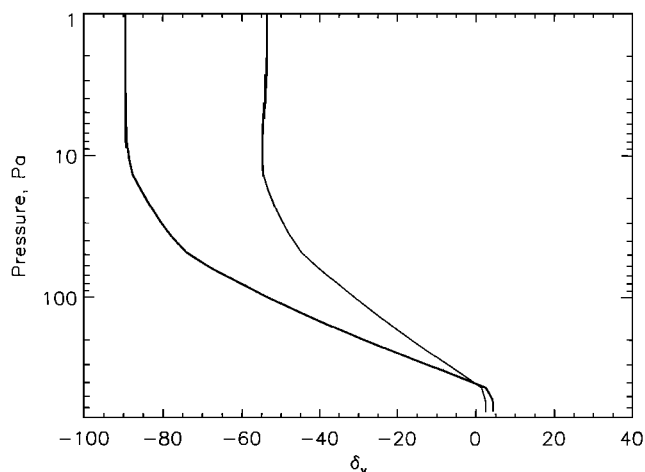


Figure 1. Vertical profile of the depletion factor δ_v of HDO with respect to H_2O due to preferential condensation of HDO on icy grains. The thin curve is for a fractionation factor α constant below 230 K, while the thick curve (more realistic) is for a value of α extrapolated for temperatures lower than 230 K, the lowest-temperature laboratory measurements. Note that HDO is depleted by a factor of 10 above 10 pascal pressure level and slightly enriched near the surface (below 300 pascal).

photodissociation is producing H_2 (and HD), explaining the low content of HD and D at 100 km. Such a depletion of HDO is indeed observed just above the terrestrial tropopause: the $\text{HDO}/\text{H}_2\text{O}$ ratio is only 33% of its value in sea water [Moyer *et al.*, 1996]. Such water vapor saturation effects may similarly affect D/H ratios in the atmosphere of Mars. The condition is that the hygropause (the level at which H_2O saturates) be below or around the peak of the photolysis rate, because it may be expected that the $\text{HDO}/\text{H}_2\text{O}$ ratio will also decrease substantially at the hygropause, marking a “Deuteropause.”

A detailed time-dependent physical model of cloud formation in the atmosphere of Mars was developed at Service d’Aéronomie to prepare future space missions to this planet (F. Montmessin *et al.*, New insights into Martian dust distribution and water ice cloud microphysics, submitted to *Journal of Geophysical Research*, 2001). It includes a size distribution of dust particles, serving as condensation nuclei, initial vertical profiles of temperature, H_2O , and eddy mixing; the growth of icy particles and their sedimentation and possible resublimation are described in the model (see Appendix A for a short description). As a spin-off of this model, the condensation of HDO was also included in the model. It is not the purpose of this paper to describe in detail the results of this model for the various conditions of Mars, but rather to concentrate on one typical example.

Figure 1 shows the computed depletion δ_v of HDO due to CEFE in the case of a cold temperature profile and $10 \mu\text{m}$ precipitable micron (pr) of H_2O . This particular atmospheric profile corresponds to Mars aphelion conditions during northern late spring/early summer at low latitude with a low dust loading described by a vertical optical thickness of 0.2, as found by Clancy *et al.* [1996]. The depletion of HDO in the vapor phase is defined as

$$\delta_v = 100 \times \frac{(\text{HDO}/\text{H}_2\text{O})_{\text{vapor}} - 1.7 \times 10^{-3}}{1.7 \times 10^{-3}}, \quad (2)$$

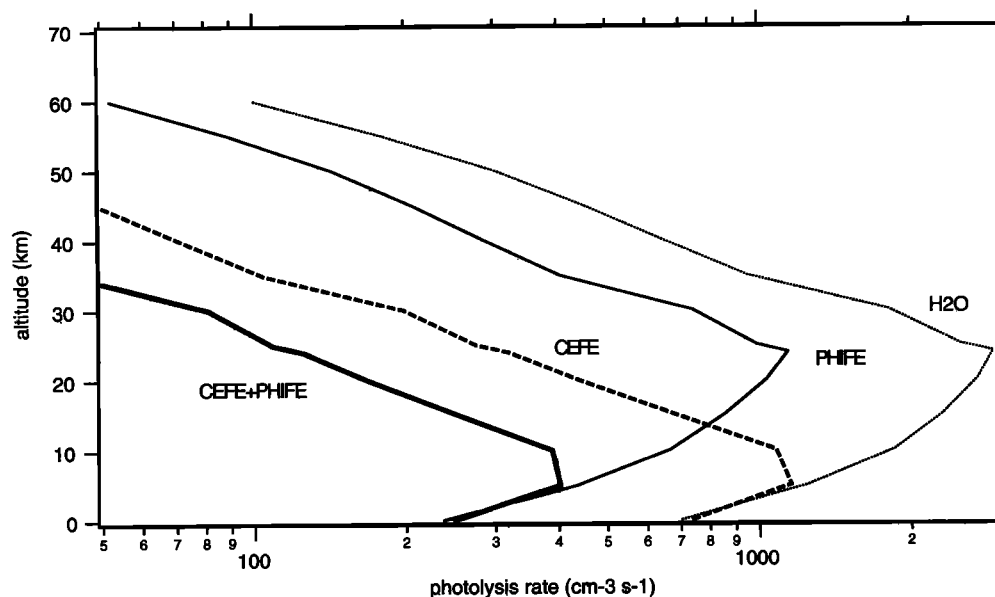


Figure 2. The dotted line is the photolysis rate of H_2O in the atmosphere of Mars (in molecules $\text{cm}^{-3} \text{s}^{-1}$) as taken from *Cheng et al.* [1999] as a function of altitude. The curve labeled PHIFE (also from *Cheng et al.* [1999]) is the photolysis rate of HDO, if its mixing ratio were equal to the mixing ratio of H_2O . It illustrates the effect of a lower photodissociation cross section of HDO. The dashed curve labeled CEFE illustrates the effect of the HDO depletion of Figure 1. The thick curve labeled CEFE+PHIFE indicates their combined effect. The integrated photolysis rate of this last curve is 9.5 times lower than for H_2O , which explains why there are so few deuterium atoms in the upper atmosphere of Mars.

where 1.7×10^{-3} is the bulk ratio of HDO/ H_2O measured in the atmosphere of Mars. A negative value of δ_v indicates a depletion of HDO relative to H_2O . There are two curves of δ_v , which correspond to two different values of the fractionation coefficient $\alpha = (\text{D}/\text{H})_{\text{ice}}/(\text{D}/\text{H})_{\text{vapor}}$. This is because the laboratory measurements [*Merlivat and Nief, 1967*] of α were made only between $T = 270$ and 240 K, while the Mars temperature profile needs estimates of α down to 140 K. The thick curve is for an extrapolation of the curve $\alpha(T)$ established for laboratory measurements (α increases with decreasing temperature and increasing altitude), while the thin curve is when α is limited to 1.24 for all temperatures below 230 K. Indeed, quantum mechanics calculations have validated the laboratory measurements and their extrapolation at lower temperature. This underestimates the effect of isotopic fractionation, and the thick curve is certainly more realistic.

For this particular profile the H_2O saturation altitude was found to be $7\text{--}8$ km, or a pressure level of 350 pascal (or 3.5 mbar). Corresponding to this hygroscopic cold trap, the deuterium depletion δ_v decreases rapidly with altitude, with a depletion factor of 10 ($\delta_v = -90\%$) above 15 pascal (0.15 mbar, or 21.5 km). This is actually still below the peak altitude (25 km) for the photolysis rate of HDO (and H_2O) as computed by *Cheng et al.* [1999] from the photochemical model of *Nair et al.* [1994], as illustrated in Figure 2. The H_2O photolysis rate as a function of altitude is taken from *Cheng et al.* [1999], as well as the HDO photolysis rate, computed as if the mixing ratio of HDO were equal to the mixing ratio of H_2O as a function of altitude. The difference between the HDO curve and the H_2O curve is therefore entirely due to the PHIFE. The curve labeled CEFE represents what would be the photolysis rate of HDO if the UV cross sections were equal for H_2O and HDO and if there were as much HDO as H_2O at ground level.

It is obtained by multiplying the H_2O photolysis curve by the ratio $(\text{HDO}/\text{H}_2\text{O})_{\text{vapor}}/1.7 \times 10^{-3} = \delta_v/100 + 1$. This CEFE curve illustrates the fact that HDO is seriously depleted by fractionation in the region of photolysis and production of HD. The thin curve marked CEFE+PHIFE yields the combined effect of CEFE and PHIFE on the photolysis of HDO in the atmosphere of Mars as a function of altitude. It is obtained by multiplying the CEFE curve by the ratio $\text{PHIFE}/\text{H}_2\text{O}$, since the photolysis rate of HDO is proportional to the density of HDO. The four curves of Figure 2 have been integrated vertically (up to 60 km) to measure the respective magnitudes of CEFE and PHIFE. The total photolysis rate of H_2O is 9×10^9 molecules $\text{cm}^{-2} \text{s}^{-1}$; the integral of curve PHIFE is a factor of 2.47 below, the curve CEFE is a factor of 3.47 below the H_2O integral, while the combined CEFE+PHIFE is a factor of 9.5 below the H_2O curve. It clearly points out the importance of the two effects for the depletion of D atoms in the upper atmosphere of Mars, CEFE being a little larger than PHIFE (at least for this particular temperature H_2O profile).

3. Implications of CEFE for the Deuterium Fractionation in the Atmosphere of Mars

We should also quote a recent cloud modeling [*Fouchet and Lellouch, 2000*] of this vapor pressure isotope fractionation, which shows exactly what we suggest here, though it is simpler and was undertaken for a different purpose: the possible bias of HDO measurements on Mars. The bias is found negligible for IR measurements, while it might amount to 10% for disk average millimetric HDO lines. Their model was a more simplistic model than ours: two simple ideal cases are considered. A closed cloud system [*Dansgaard, 1964*], where the condensed and vapor phases ascend together in the air parcel, induces the

smallest deuterium depletion. An open cloud system [Dansgaard, 1964], where the icy grains leave the cloud by sedimentation just after their formation, induces the largest deuterium depletion.

Clearly, the CEFE depends very much on the temperature profile, the H₂O profile, the dust loading (to provide condensation nuclei), and the sedimentation velocity. When folded with the PHIFE, which also depends on the solar zenith angle, it results in a complicated picture of the production of HD from HDO. The particular atmospheric profile that was taken in this study holds for Mars aphelion conditions during northern late spring/early summer at low latitude [Clancy *et al.*, 1996]. According to these authors, it is when the hygropause is at its lowest altitude (at midlatitude). However, we note from their Figure 3 that the hygropause (and corresponding Deuteropause) will be below 20 km, well below the peak altitude for the photolysis rate. Therefore integration over the whole year and all latitudes will possibly (but not surely) give a lower magnitude of CEFE, but not by a large amount. On the other hand, aphelion, although extremely propitious for low-altitude clouds, is not the preferred season for water ice clouds on Mars. Polar clouds during winter, especially the northern one, are assumed to be located at even lower altitude, a case not studied yet. Their complex nature, due to the additional condensation of carbon dioxide, makes them beyond the scope of the present study, but they clearly call for an enhanced fractionation effect on the basis of a full Martian year study.

The fact that HST L α observations imply that the partitioning factor R is only 0.09 instead of 1.6 calls for an average depletion of HDO integrated photolysis rate of $1.6/0.09 = 18$, while we found a factor of only 9.5. However, the estimate of this partitioning factor R from the HST results depends on the assumed variation of the eddy diffusion coefficient with solar activity [Krasnopolsky, 2000]. This assumption notwithstanding, our proposed scheme of a preferential cold trap for HDO gives a simple explanation, when combined with PHIFE, for what appeared before to be a puzzle: the great depletion of D atoms in the upper atmosphere of Mars. This severe depletion has the immediate consequence that the escape rate of D atoms is reduced by the same factor of 11, with respect to the nondepleted case. In fact, we are very near the limiting case of no escape of D at all, which allows us to derive immediately the initial water reservoir from the present reservoir: a multiplication by the present HDO enrichment, a factor of 6. Indeed, this cold trap for deuterium (or Deuteropause) is likely to have existed through aeons, inhibiting D escape throughout the life of Mars. (A more exact calculation implies an escape flux ratio of D and H of 0.02, and the integration in time gives 6.22 for the ratio of initial to present reservoir).

Given the present estimate of the ice in polar caps [Zuber *et al.*, 1998], this present water reservoir represents ~ 9 m of water uniformly spread over the Martian surface, and an initial reservoir of 55 m. The difference, 46 m, must have escaped to space. This is less than the maximum possible escape as computed from models [Kass and Yung, 1995], 80 m, by a factor of 2. However, this maximum estimate is obtained in extreme conditions and not too likely conditions, while 46 m seems more reasonable (the estimate for Earth is 3 m). Therefore it indicates that there is, at the present time, little room for a water reservoir (other than the ice caps) of significant amount in Mars capable of exchanging with the ice cap-atmosphere system. There may be ice in the permafrost, but it should be unable to exchange with the atmosphere.

Our proposed scheme, in order to be valid, needs the bulk of H₂O and HDO photolysis by solar UV to occur at altitudes higher than the altitude of the cold trap for HDO. This is clearly the case for Earth but might not always be the case for Mars. In Figure 1 the HDO cold trap is located at 7 km, but it varies with the temperature profile and the column amount of H₂O from 1 to 30 km. For a given temperature profile it is lowest when the H₂O column amount is highest, while the UV solar flux, absorbed by CO₂ and aerosols, is rapidly increasing with altitude (in all conditions). The vertical distribution of the H₂O photolysis rate is extremely sensitive to the temperature profile. In order to get a detailed estimate of what fraction of the total photolysis rate occurs above the altitude of the cold trap, it would certainly need more than a one-dimensional (1-D) model in average conditions, calling rather for a 3-D atmospheric model combining the dynamics, the distribution of H₂O (and HDO), and the photochemistry of the atmosphere of Mars. What can be said briefly is that the timescale associated with HDO depletion through condensation follows the one of water vapor depletion at cloud level. Michelangeli *et al.* [1993] pointed out that the typical timescale for condensation does not exceed several hours under Martian conditions. Compared to the vertical timescale within Hadley circulation (5–10 days [Clancy *et al.*, 1996]), fractionation through condensation may be considered as quasi-instantaneous and should clearly dominate the advective influence on the HDO vertical profile. The D/H ratio in the upper part of the atmosphere is governed by several influences which would deserve a complete 3-D modeling, including all the processes involved in the deuterium upward flux. As already mentioned, aphelion is not the only season assumed to favor CEFE from a global point of view. Also, the lifetime of H₂ and HD, ultimate providers of H and D in the upper atmosphere, is longer than one Martian year: Therefore we would not expect an orbital variation of D Lyman alpha emission. Rather, such an orbital variation could better be observed directly on the HDO/H₂O ratio at 10–40 km of altitude with an orbiting solar occultation instrument.

In terms of the D/H variations in the terrestrial atmosphere, it could be pointed out that the D L α emission from the upper atmosphere has been clearly measured from space shuttle measurements [Bertaux *et al.*, 1993], indicating a D/H ratio at 100 km similar to the D/H ratio in oceans, and this in spite of the existence of a similar cold trap for HDO at the troposphere-stratosphere interface. This is easily explained by the fact that deuterated methane CH₃D can go through this interface without condensing. Therefore D atoms can rise in the stratosphere. Above the tropopause, CH₄ and CH₃D are oxidized by reactions with OH and O (1D), ending after a complex chain of reactions into H₂O and H₂, and their deuterated isotopes HDO and HD. These isotopes are providing the deuterium atoms that are finally observed in L α emission above 100 km. The substantial amount of D atoms found in the upper atmosphere of the Earth is therefore connected to the existence of methane in Earth's atmosphere. Since methane on Earth is essentially a gas of biological origin (either present or fossil), the presence of a substantial amount of deuterium in the upper atmosphere of Earth is connected to the presence of life on Earth. At this stage, however, it would be preposterous to conclude, from the relative lack of deuterium in the upper atmosphere of Mars, that there is an absence of life on Mars.

Appendix A: Microphysical Model

Here we briefly summarize the key elements used to model cloud formation under Martian conditions. This Eulerian model allows only one-dimensional simulations and is based on a previous one used to describe aerosol formation in the atmosphere of Titan [Cabane *et al.*, 1992]. The atmosphere of Mars is divided into 30 equally thick slabs from 0 to 60 km of altitude (upper boundary of the model). Four different quantities (densities of dusty and icy particles as well as H₂O vapor and its isotope HDO) are tracked all through the atmospheric column, where they experience all the microphysical processes assumed to occur on Mars. Particles' number densities are stored at each altitude and for 60 size bins. Ice crystals are formed from the heterogeneous nucleation of small icy embryos onto the surface of the insoluble Martian aerosols. The governing law of heterogeneous nucleation is given by [Pruppacher and Klett, 1978]

$$J_{\text{nuc}} \sim A r_p^2 \exp\left(\frac{-\Delta F^*}{kT}\right),$$

where A is a prefactor of the order of $10^{18} \text{ m}^{-2} \text{ s}^{-1}$, r_p is the radius of the dust nucleus, k is the Boltzman's constant, T the temperature of the environment, and ΔF^* is the free energy term of water embryo formation. J_{nuc} is expressed in s^{-1} . When the bottleneck barrier set by nucleation is overcome, crystal growth by water molecules diffusion takes place (condensation). It is commonly described in terms of a radius variation per unit of time since crystals' shapes are approximated by a sphere representation. If r is the radius of the crystal, then, following Pruppacher and Klett [1978],

$$r \frac{dr}{dt} = \frac{S - S_{\text{eq}}}{R_D + R_H},$$

where S is the saturation ratio of water, S_{eq} is the saturation ratio at equilibrium (usually assumed to be 1), and R_D and R_H are the resistances induced by molecular diffusion and latent heat release, respectively. Depending on the sign of $S - S_{\text{eq}}$, the radius variation implies either condensation or evaporation. The former process, when strong enough, permits the dust core to be released in the atmosphere, a point also included in the present model. Given the low population of suspended dust particles, particle aggregation through coagulation is known to be insignificant [Michelangeli *et al.*, 1993]. Because of gravity, particles are constrained to fall with a velocity given by Fuchs [1964]:

$$\omega = \frac{2g\rho}{9\nu_a} \left\{ 1 + Kn \left[1.246 + 0.42 \exp\left(\frac{-0.87}{Kn}\right) \right] \right\} r^2,$$

where ω is the settling velocity, g is gravity, ρ is the particle density, ν_a is the dynamic viscosity of air, and Kn is the Knudsen number. Vertical diffusion implied by air mass dynamics is also accounted for by representing it with the eddy mixing coefficient K_d . This phenomenon affects, this time, either vapor species (like H₂O vapor or HDO) or suspended particles. A standard value of $100 \text{ m}^2 \text{ s}^{-1}$ for K_d is chosen and likely represents the dynamics activity encountered in the Hadley cell during aphelion [Clancy *et al.*, 1996]. Finally, we shall mention the way HDO sustains fractionation during condensation process. Indeed, the intensity of fractionation is described from the following relation [Merlivat and Nief, 1967], where α is the fractionation coefficient:

$$\ln \alpha = \frac{16288}{T^2} - 0.0934.$$

We then determine the amount of condensed HDO since α was experimentally obtained by Merlivat and Nief [1967] as the ratio of the HDO fraction in water vapor to that in water ice. Our representation of fractionation is akin to the Rayleigh model of Dansgaard [1964] describing the direct transformation of water vapor into its solid phase.

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